COLLEGE

CHEMISTRY

Intermediate Part I

11

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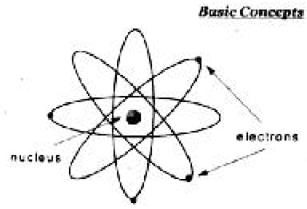
Chapter-1 Basic Concepts



ATOM

Atom is the smallest particle of an element, which can take part in a chemical reaction.

- The atoms of He, Ne (noble gases) can exist independently.
- The atoms of hydrogen, nitrogen and oxygen cannot exist independently.
- Atom is now further divisible into sub-atomic particles.
- More than 100 sub-atomic particles are thought to exist in an atom.
- A few sub-atomic particles are electron, proton, neutron, hypron, neutrino, antineutrino etc.
- Electrons, protons and neutrons are the fundamental particles of atom.

History of Atom

Earlier Concept and Greek Philosopher's Work

- Earlier it was though that matter is made up of simple, indivisible particles.
- Greek philosophers thought that matter could be divided into smaller and smaller particles. Thus a basic unit could be reached which cannot be further sub-divided.
- Democritus (460–370 B.C.) called the indivisible particles of matter as atoms.
- The word atom is derived form Greek word 'atomos' means 'indivisible'.
- The concepts of Greek Philosophers were not based on experimental proofs.

Late 17th Century work

- In late 17^{th} century, the quantitative composition of substances was studied. It showed that few elements are present in many different substances.
- It was also studied that how elements combine to form compounds and compounds could be broken into elements.

Dalton's Work

- In 1808, John Dalton, an English School teacher, explained law of conservation of mass and law of definite proportion on the basis of concept of atoms. He developed an atomic theory.
- According to main postulate of Dalton's theory, all matter is composed of atoms of different elements, which differ in their properties.

Berzelius Work

- A Swedish chemist J. Berzelius (1779 – 1848) determined the atomic masses of elements. A number of his values are very close to modern values of atomic masses.
- Berzelius developed the system of giving symbols to elements.

Evidence for an Atom

- ***Use of Optical Microscope:***

Ordinary optical microscope can measure the size of an object up to or above 500 nm. Therefore, a clear and accurate image of object that is smaller than the wavelength of visible light cannot be obtained. Since atoms are much smaller than 500 nm, So, they cannot be seen with optical microscope.

- ***Use of Electron Microscope:***

A direct evidence of atom can be obtained by an electron microscope. It uses a beam of electrons instead of visible light. The wavelength of electrons is much shorter than visible light and is suitable to see extremely small objects. A less clear picture of atoms is obtained by an electron microscope.

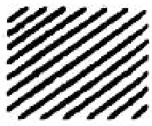


Fig: Electron microscope photograph of graphite

Example: The figure shows an electron microscopic photograph of a piece of graphite. It has been magnified about 15 million times. The bright bands in the figure are layers of carbon atoms.

- ***Use of X-rays:***

In the 20th century, X-ray work has shown that

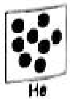
(i) the diameters of atoms are approximately 2×10^{-10} m or 0.2×10^{-9} m or 0.2 nm.
(ii) Masses of atoms range from 10^{-27} to 10^{-25} kg.

- The masses of atoms are often expressed in atomic mass units (amu).
  1 amu $= 1.661\times10^{-27}$ kg $= 1.661\times10^{-27}$ g
- A full stop may have two million atoms present in it.

MOLECULE

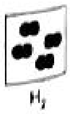
The smallest particle of a pure substance, which can exist independently, is called a molecule.

Atomicity (Monoatomic and Polyatomic molecules)



He

- The number of atoms in a molecule is called its atomicity.
- A molecule containing one atom is called a monoatomic molecule.
- A molecule containing two or more atoms is called a polyatomic molecule.
  The polyatomic molecules containing two or three atoms are called diatomic and triatomic molecules respectively.



H_2

Examples:

- Monatomic molecules: He, Ne, other noble gases
- Polyatomic molecules: H_2, CO, O_2, CO_2, NH_3 etc.

Homo-atomic and Hetero-atomic molecules

(Difference between molecule of an element and compound)

- Molecules of elements may contain one, two and three same type of atoms. e.g. He, Cl_2, O_3, P_4, S_8. These are called homo-atomic molecules.
- Molecules of compounds consist of different kind of atoms. e.g. HCl, NH_3, H_2SO_4, $C_6H_{12}O_6$. These are called hetero-atomic molecules.

Micromolecules and Macromolecules

- Molecules have bigger size than atoms. The size of molecule depends upon
  (i) number of atoms in a molecule.
  (ii) shape of molecule.
- Molecules containing fewer numbers of atoms and are small in size are called micromolecules.
  Examples: CO_2, NH_3, H_2SO_4, $C_6H_{12}O_6$ etc.
- Molecules containing large number of atoms and are large in size are called macromolecules.
  Example: **Haemoglobin:** It is found in blood. It helps to carry oxygen from lungs to all parts of body. One molecule of haemoglobin is made up of about 10,000 atoms. It is 68,000 times heavier than a hydrogen atom.

ION

Ions are those species which carry either positive or negative charge.

These are of two types

Positive Ions

Ions which carry positive charge are called positive ions.

- When an atom of an element loses one or more electrons, positive ions are produced.
  $$A \rightarrow A^+ + e^-$$
- The removal of electrons from an atom requires energy, hence formation of positive ion is an endothermic process.
- Positive ions are called cations.
- An atom may lose one, two or three electrons to form monopositive, dipositive or tripositive ions respectively.
- The most common positive ions are formed by the metal atoms.

Examples:

Na^+, K^+, Ca^{2+}, Al^{3+}, Fe^{3+}, Sn^{4+} etc.

Negative Ions

Ions which carry negative charge are called negative ions.

- When an atom of an element picks up one or more electrons, negative ions are produced.

$$B + e^- \longrightarrow B^-$$

- The addition of one electron in an atom ususally results in release of energy. It is due to the attraction between nucleus and incoming electron. Hence formation of uninegative ion is an exothermic process.
- An atom may gain two electrons to form a dinegative ion. However, it will be an endothermic process due to repulsion between uninegative ion and second incoming electron.
- Negative ions are called Anions.

Examples:

F^-, Cl^-, Br^-, S^{2-}

NOTE:

- Negative ions may consist of group of atoms e.g. CO_3^{2-}, $Cr_2O_7^{2-}$, MnO_4^-, PO_4^{3-}, SO_4^{2-} etc.
- Positive ions containing group of atoms are rare e.g. NH_4^+, H_3O^+ and carbocations in organic chemistry etc.
- The cations and anions have completely different properties from their corresponding neutral atoms

Molecular Ion

The ion formed due to loss or gain of electrons by a molecule is called a molecular ion

Examples:

CH_4^+, CO^+, N_2^+ etc.

Abundance: Cationic molecular ions are more abundant than anionic molecular ions.

Generation: Molecular ions are generated by passing high energy electron beam, α-particles or X-rays through a gas.

Application: Breaking of molecular ions from natural product can give important information about structure of the compound.

RELATIVE ATOMIC MASS

Definition: It is the mass of an atom of an element as compared to the mass of an atom of carbon taken as 12.

Unit: Atomic mass is expressed in ATOMIC MASS UNITS, denoted by amu.

Atomic mass unit is defined as

The $\frac{1}{12}$ of the mass of one atom of carbon is called 1 amu.

$$1\ amu = 1.661 \times 10^{-27}\ kg = 1.661 \times 10^{-24}\ g$$

Examples:

On carbon-12 scale, the relative atomic mass of $^{12}_{6}C$ is 12.0000 amu and that of $^{1}_{1}H$ is 1.0078 amu.

Why relative atomic mass unit scale is used?

Atomic masses of atoms are very small. These cannot be measured by a physical balance. Thus relative atomic mass unit scale is used.

Table: Relative Atomic Masses of a few elements

Elements	Relative Atomic Mass (amu)	Elements	Relative Atomic Mass (amu)
H	1.00794	Cl	35.453
O	15.9994	Cu	63.546
Ne	20.1797	U	238.0289

ISOTOPES

John Dalton thought that all the atoms of an element were similar. However, Soddy showed that atoms of the same element may be different.

Definition: Atoms of the same element, having same atomic number but different atomic masses are called isotopes

The phenomenon of isotopy was discovered by Soddy.

Properties of Isotopes

- Isotopes have same number of electrons and protons but different number of neutrons in their nuclei
- Isotopes of an element have different physical properties due to different number of neutrons in their nuclei.
- Isotopes of an element have same chemical properties because they have same number of valence electrons. During chemical reactions valence electrons are involved.
- Isotopes have same position in the periodic table since they have same atomic number.

Examples

(i) Carbon has three isotopes written as ${}^{12}_{6}C$, ${}^{13}_{6}C$, ${}^{14}_{6}C$ and expressed as C–12, C–13, C–14, having 6, 7 and 8 neutrons in their nuclei respectively.

(ii) Hydrogen has three isotopes

${}^{1}_{1}H$ Protium ${}^{2}_{1}H$ Deuterium ${}^{3}_{1}H$ Tritium

Oxygen has three isotopes, Nickle has five isotopes, Calcium has six isotopes, Palladium has six isotopes, Cadmium has nine isotopes, tin has eleven isotopes etc.

Relative Abundance of Isotopes

- The natural occurrence of different isotopes of an element is called their relative abundance. Isotopes of all the elements have their own natural abundance.
- The masses and abundance of isotopes of an element can be determined by Mass Spectrometry.
- The properties of elements are mostly like that of most abundant isotope of that element.

Facts about Relative abundance of isotopes:

- There are above 280 different isotopes that occur in nature.
- Out of 280, there are about 40 radioactive isotopes
- Besides these, about 300 unstable radioactive isotopes have been produced through artificial disintegration in nuclear reactor.
- Elements with odd atomic number almost have maximum two stable isotopes
- Elements with even atomic number usually have many isotopes
- Isotopes with mass number of four or some multiple of four are more abundant e.g. ${}^{16}O$, ${}^{24}Mg$, ${}^{28}Si$, ${}^{40}Ca$, ${}^{56}Fe$ form nearly 50% of the earth crust.
- Out of 280 natural isotopes, 154 have even mass number and even atomic number

Monoisotopic Elements

Elements having only one isotope are called mono-isotopic elements.

Examples:

Arsenic, Fluorine, Iodine, Gold etc have only single isotope.

Table Natural abundance of some common isotopes

Elements	Isotope	Abundance (%)
Hydrogen	${}^{1}H$, ${}^{2}H$	99.985, 0.015
Carbon	${}^{12}C$, ${}^{13}C$	98.893, 1.107
Nitrogen	${}^{14}N$, ${}^{15}N$	99.634, 0.366
Oxygen	${}^{16}O$, ${}^{17}O$, ${}^{18}O$	99.759, 0.037, 0.204
Sulphur	${}^{32}S$, ${}^{33}S$, ${}^{34}S$, ${}^{36}S$	95.0, 0.76, 4.22, 0.014
Chlorine	${}^{35}Cl$, ${}^{37}Cl$	75.53, 24.47
Bromine	${}^{79}Br$, ${}^{81}Br$	50.54, 49.49

MASS SPECTROMETRY

Mass Spectrometry is an analytical method used to measure the exact masses of different isotopes of an element

The Instrument used for this purpose is called Mass Spectrometer

- Initially Aston's mass spectrograph was used to identify isotopes on the basis of their atomic masses
- Dempster's mass spectrometer was designed for the elements found in solid state.

Method

A typical mass spectrometer consists of following parts

(1) Vaporizaiton Chamber   (2) Ionization Chamber   (3) Analyzer

(4) Electrometer (Ion Collector)   (5) Detector, Amplifier and Recorder

(1) Vaporization Chamber

The substance is first converted into vapour state. The pressure of these vapours is kept very low i.e. 10^{-6} to 10^{-7} torr.

(2) Ionization Chamber

The vapours are then passed into an ionization chamber. In this fast moving electrons are thrown upon them. As a result gaseous atoms are ionized and positive ions are produced. These positive ions have different masses due to presence of different isotopes in them.

(3) Analyzer

The analyzer separate ions on the basis of their m/e value in two steps.

(i) *Acceleration of ions:* Each positive ion has its own m/e (mass to charge) value. A potential difference (E) of 500 – 2000 volts is applied between the perforated plates to accelerate the ions. Thus ions are strongly attracted towards the negative plate.

(iii) Deflection of Ions: The ions are then passed through a strong magnetic field of strength 'H'. It deflects the ions on the basis of their m/e value. Thus, ions follow a circular path.

The mathematical relationship is

$$m/e = \frac{H^2 r}{E}$$

Where H = Strength of magnetic field,

E = Strength of electric field,

r = radius of circular path.

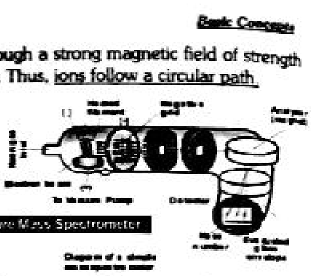


Figure Mass Spectrometer

It shows that

- By keeping '*E*' constant, if '*H*' is increased, '*r*' also increases. Thus, ions of a particular m/e value can be made to fall at different place than before.
- It can also be done by keeping '*H*' constant and by changing '*E*'.
- So, smaller the '*m/e*' value, smaller will be the '*r*' produced by magnetic field.

Hence ions with same m/e values are separated into beams of ions.

(4) Electrometer (Ion Collector)

In mass spectrometer, the separated beams of ions are passed through slit one by one. Each beam contains ions of specific m/e value. These fall on an electrometer, called ion collector. The electrometer develops electric current. The strength of current for each beam gives the relative abundance of ions.

(5) Detector, Amplifier and Recorder

In modern spectrographs, the ions strike the detector to generate current. The current is amplified and fed to the computerized recorder.

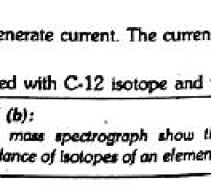
(i) Comparison with C-12: The same experiment is performed with C-12 isotope and the current strength is compared. This comparison gives the exact mass number of isotope.

> ***Exercise Q5 (b):***
> *How does a mass spectrograph show the relative abundance of isotopes of an element?*

(ii) Mass Spectrum (or Mass Spectrograph):

In mass spectrometer, the result is recorded in the form of a graph containing peaks. The relative numbers of ions are present along Y-axis (ordinate) and m/e values of ions are present along X-axis (abscissa). This is called Mass Spectrum. It gives following information

- the number of peaks gives the number of isotopes of an element
- the height of peak gives the relative abundance of isotopes
- the position of peak gives the mass number of isotopes.



Fig(1.3) Computer plotted graph for the isotopes of neon

Other techniques for separation of isotopes:

Isotopes can also be separated by following techniques on the basis of their properties.

(i) gaseous diffusion *(ii)* thermal diffusion *(iii)* distillation

(iv) ultracentrifuge *(v)* electromagnetic separation and *(vi)* laser separation etc.

Basic Principle of Mass Spectrometry

A substance is first volatilized. It is then ionized with the help of high energy beam of electrons to form gaseous positive ions. These ions are separated on the basis of their mass to charge ratio (m/e). The result is recorded in the form of peaks. The result is a graph in which m/e is plotted as abscissa (x-axis) and the relative number of ions as ordinate (y-axis). This graph is called mass spectrum. It tells about number, mass and relative abundance of isotopes.

Fractional Atomic Masses

Exercise Q5.(a)

What are the isotopes? How do you deduce the fractional atomic masses of elements from the relative isotopic abundances? Give two examples in the support of your answer?

The atomic masses of elements are written as average atomic masses. These depend upon the number of isotopes of an element, their masses and their natural abundance. Thus, most of the elements have fractional atomic masses.

Example 1.

A sample of neon is found to consist of $^{20}_{10}Ne$, $^{21}_{10}Ne$ and $^{22}_{10}Ne$ in the percentages of 90.92%, 0.26%, 8.82% respectively.

The average atomic mass of Ne is given as

$$\text{Average atomic mass} = \frac{(20\times 90.92)+(21\times 0.26)+(22\times 8.82)}{100} = 20.18$$

Hence the average atomic mass of neon is 20.18 amu

Actually, there is no individual neon atom in the sample that has a mass of 20.18 amu. However, in routine work the sample of neon is considered to have average mass of ***20.18 a.m.u.***

Example 2.

Silver has two important naturally occurring isotopes, ^{107}Ag and ^{109}Ag with relative abundances 51.84% and 48.16% respectively.

The average atomic mass of Ag is given as

$$\textit{average atomic mass} = \frac{(107\times 51.84)+(109\times 48.16)}{100} = 107.96\ amu$$

ANALYSIS OF A COMPOUND

To find the molecular formula of a compound following steps are taken.

1. All the elements present in the compound are identified. This is called qualitative analysis.
2. The mass of each element is determined in the compound. This is called quantitative analysis.
3. The mass of each element is used to calculate the percentage by mass of each element.
4. The percentage is used to determine the empirical formula of the compound
5. Finally molecular formula is obtained from empirical formula and molecular mass.

Percentage of Element in a Compound

It is the number of grams of an element present in 100g of the compound.

- ***Percentage from given amounts:*** The percentage of each element in a compound can be determined by following formula.

$$\text{Percentage of an element} = \frac{\text{Mass of the element}}{\text{Mass of the compound}} \times 100$$

- ***Percentage from Formula Mass:*** The percentage of each element in a compound can be determined theoretically from formula mass of a compound.

$$\text{Percentage of an element} = \frac{\text{Mass of the element}}{\text{Molar Mass of the compound}} \times 100$$

Example 2:

8.657 g of a compoundy were decomposed into its element and gave 5.217 g of carbon, 0.962g of hydrogen, 2.478 g of oxygen. Calculate the percentage composition of the compound under study.

Solution:

→ Mass of the given compound = 8.657g

Mass of C = 5.217g

Mass of H = 0.962g

Mass of O = 2.478g

→ Percentage of the elements can be calculated by the formula

$$\%\text{ of element} = \frac{\text{mass of the element}}{\text{mass of the compound}} \times 100$$

$$\%\text{ of C} = \frac{5.217}{8.657} \times 100 = \boxed{60.26\%}$$

$$\%\text{ of H} = \frac{0.962}{8.657} \times 100 = \boxed{11.11\%}$$

$$\%\text{ of O} = \frac{2.478}{8.657} \times 100 = \boxed{28.62\%}$$

Empirical Formula

The formula, which shows the simplest whole number ratio between atoms of a compound, is called empirical formula.

Examples:

Empirical formula of hydrogen peroxide is HO. It shows that simplest whole number ratio between H and O is 1:1.

Similarly empirical formulas of glucose and benzene are CH_2O and CH respectively.

Steps to Determine the Empirical Formula

(i) Determine the percentage composition of each element in a substance.

(ii) Divide the percentage of each element by its atomic mass to get number of gram atoms (moles).

(iii) Divide the moles of each element by the smallest number of moles to get atomic ratios.

(iv) If atomic ratios are not in simple whole number, then multiply with a small suitable number to get whole number ratio.

Thus empirical formula is obtained.

Molecular Formula

The formula, which shows the exact number of atoms of each element present in one molecule of a compound, is called molecular formula.

It is based on an actual molecule

Examples:

Molecular formulas of benzene and glucose are C_6H_6 & $C_6H_{12}O_6$ respectively.

Relationship Between Empirical and Molecular Formula

(i). Molecular formula may be the multiple of empirical formula. For many compounds empirical and molecular formulas are different.

Examples: Empirical formulas of benzene and glucose are CH and CH_2O respectively. However, their molecular formulas are C_6H_6 and $C_6H_{12}O_6$ respectively.

This relationship can be expressed as

Molecular formula = *n* (empirical formula)

where, 'n' is an integer and its value is 1, 2, 3....

The 'n' shows the ratio of molecular mass and empirical formula mass.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}}$$

(II) The compounds may have same empirical and molecular formulas.

Examples: NH_3, H_2O, CO_2, $C_{12}H_{22}O_{11}$ etc. For such compounds value of 'n' is unity.

Difference between Empirical and Molecular Formula

	Empirical Formula		Molecular Formula
1	It shows the simplest whole number ratio between atoms of a compound.	1	It shows exact number of atoms of each element present in one molecule of a compound.
2	Both ionic and covalent compounds have empirical formula	2	Ionic compounds do not have molecular formula.
3	It is based on formula unit which may or may not exist independently	3	It is based on an actual molecule which exist independently
4	It is obtained from percentage composition of elements in a compound.	4	It is obtained from empirical formula by using the relationship. Molecular formula = n (empirical formula)
5	Examples: Empirical formulae of glucose and benzene are CH_2O and CH respectively.	5	Examples: Molecular formulae of glucose and benzene are $C_6H_{12}O_6$ and C_6H_6 respectively.

EMPIRICAL FORMULA FROM COMBUSTION ANALYSIS

Combustion Analysis:

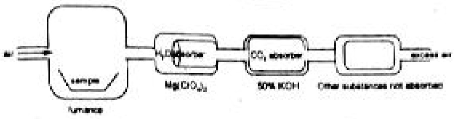
It is an experimental procedure by which amounts of various elements present in the given amount of a compound are determined by burning.

Organic compounds containing only C, H and O are analyzed by combustion analysis.

Method:

- A weighed quantity of the compound is burned, in a combustion tube. The combustion tube is fitted in a furnace.
- Oxygen is supplied to burn the compound.
- Hydrogen and carbon contained in the compound are converted to H_2O & CO_2 respectively.

$$C \,\&\, H \text{ in sample} + O_2 \longrightarrow CO_2 + H_2O$$



- In combustion analysis, the water vapours formed are absorbed in magnesium perchlorate [***$Mg(ClO_4)_2$***]
- The CO_2 is absorbed in ***50% KOH*** solution.
- The increase in masses of these absorbers gives the masses of H_2O and CO_2 produced.
- Other absorbers can be used for other products of combustion.
- The amount of oxygen is determined by the method of difference.
- ***Formulas for calculations:*** For a compound containing C, H & O only, the formulas for percentages are

$$\% \text{ of C} = \frac{\text{mass of } CO_2}{\text{mass of organic compound}} \times \frac{12}{44} \times 100$$

$$\% \text{ of H} = \frac{\text{mass of } H_2O}{\text{mass of organic compound}} \times \frac{2.016}{18} \times 100$$

$$\% \text{ of oxygen} = 100 - (\,\% \text{ of carbon} + \% \text{ of hydrogen})$$

Example 3:

Ascorbic acid (vitamin C) contains 40.92% carbon, 4.58% hydrogen and 54.5% of oxygen by mass. What is the empirical formula of the ascorbic acid?

*(Gujranwala Board, **2010**: Multan Board, **2007**: Bahawalpur Board, **2011**)*

Solution:

Element	%	No. of gram atoms	Atomic Ratio
C	40.92	$\frac{40.82}{12} = 3.41$	$\frac{3.41}{3.41} = 1$
H	4.58	$\frac{4.58}{1.008} = 4.54$	$\frac{4.54}{3.41} = 1.33$
O	54.50	$\frac{54.5}{16} = 3.41$	$\frac{3.41}{3.41} = 1$

Multiply atomic ratio by 3 to get values in simple whole numbers.

$$C : H : O = 3(1 : 1.33 : 1) = 3 : 4 : 3$$

Thus the empirical formula for ascorbic acid is $\boxed{C_3H_4O_3}$

Example 4:

A sample of liquid containing carbon, hydrogen and oxygen only was subjected to combustion analysis. 0.5439 g of the compound gave 1.039 g of CO_2, 0.6369 g of H_2O. Determine the empirical formula of the compound.

Solution:

Mass of organic compound = 0.5439g

Mass of CO_2 = 1.039g

Mass of H_2O = 0.6369g

Thus Percentage of C $= \frac{1.039}{0.5439} \times \frac{12}{44} \times 100 = 52.10\%$

Percentage of H $= \frac{0.6369}{0.5439} \times \frac{2.016}{18} \times 100 = 13.12\%$

Percentage of O $= 100 - (52.11 + 13.11) = 34.78\%$

Element	% age	No. of gram atoms	Atomic Ratio	Empirical Formula
C	52.10	$\frac{52.10}{12} = 4.34$	$\frac{4.34}{2.17} = 2$	
H	13.12	$\frac{13.12}{1.008} = 13.02$	$\frac{13.02}{2.17} = 6$	C_2H_6O
O	34.78	$\frac{34.78}{16} = 2.17$	$\frac{2.17}{2.17} = 1$	

Thus the empirical formula for the organic compound is $\boxed{C_2H_6O}$

Example 5: The combustion analysis of an organic compound shows it to contain 65.44% carbon, 5.50% hydrogen and 29.06% of oxygen. What is the empirical formula of the compound? If the molecular mass of this compound is 110.15. Calculate the molecular formula of the compound.

*(D.G. Khan Board, **2010**: Faisalabad Board, **2011**: Gujranwala Board, **2005, 2007**: Multan Board, **2011**: Rawalpindi Board, **2010, 2011**)*

Solution:

Element	% age	No. of gram atoms	Atomic Ratio	Empirical Formula
C	65.44	$\frac{65.44}{12} = 5.45$	$\frac{5.45}{1.82} = 3$	
H	5.50	$\frac{5.50}{1.008} = 5.45$	$\frac{5.45}{1.82} = 3$	C_3H_3O
O	29.06	$\frac{29.06}{16} = 1.82$	$\frac{1.82}{1.82} = 1$	

Thus the empirical formula is C_3H_3O.

To determine the molecular formula, first calculate the empirical formula mass.

Empirical formula mass of $C_3H_3O = 12\times3 + 1.008\times3 + 16\times1 = 55.05\ g\ mol^{-1}$

Molecular (or molar) mass of the compound $= 110.15\ g\ mol^{-1}$

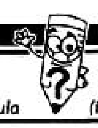
$$n = \frac{\text{molecular mass of compound}}{\text{empirical formula mass of compound}} = \frac{110.15}{55.05} = 2$$

Thus Molecular formula $= n$ (empirical formula)

$= 2\ (C_3H_3O)$

$= \boxed{C_6H_6O_2}$

MOLE



Exercise Q9:

Define the following terms and give three example of each.

(i) Gram atom (ii) Gram molecular mass (iii) Gram formula (iv) Gram ion

Mole

The atomic mass, molecular mass, formula mass or ionic mass of the substance expressed in grams is called a mole of the substance.

$$\text{Number of moles} = \frac{\text{Given Mass (in grams)}}{\text{Molar mass}}$$

Examples:

Element:	1 mole of carbon	= 12.000 g
Molecular compound:	1 mole of water	= 18 g
Ionic compound:	1 mole of NaCl	= 58.5 g
Ionic species:	1 mole ion of OH^-	= 17 g

For each type of substance mole can be defined as

Gram Atom (For Elements)

The atomic mass of an element expressed in grams is called one gram atom or one gram mole or simply a mole of that element.

Formula:

$$\text{Number of gram atoms or moles of an element} = \frac{\text{Mass of element in grams}}{\text{Atomic mass of an element}}$$

Examples:

1 gram atom of hydrogen = 1.008 g
1 gram atom of carbon = 12.000 g
1 gram atom of Magnesium = 24 g
1 gram atom of Uranium = 238 g

Thus <u>one gram atoms of different elements have different masses.</u>

So, 1 atom of Mg is two times heavier than one atom of carbon.

Gram Molecule (For Molecular compounds)

The molecular mass of a substance expressed in grams is called one gram molecule or one gram mole or simply a mole of that substance.

Formula:

$$\text{Number of gram molecules or moles of a molecular substance} = \frac{\text{Mass of molecular substance in grams}}{\text{Molecular mass of a molecular substance}}$$

Examples:

1 gram molecule of water = 18 g
1 gram molecule of H_2SO_4 = 98 g
1 gram molecule of sucrose = 342 g

Thus <u>one gram molecule of different molecular substances have different masses.</u>

Gram Formula (For Ionic compounds)

The formula mass of an ionic compound expressed in grams is called one gram formula or one gram mole or simply a mole of that substance.

Formula:

$$\text{Number of gram formulas or moles of an ionic substance} = \frac{\text{Mass of ionic substance in grams}}{\text{Formula mass of an ionic substance}}$$

Examples:

1 gram formula of NaCl = 58.5 g
1 gram formula of $AgNO_3$ = 170 g
1 gram formula of Na_2CO_3 = 106 g

NOTE: Ionic compounds do not have molecular mass

Since ionic compounds do not exist in molecular form, therefore, term molecular mass is not used for them. In ionic compounds the sum of atomic masses of individual ions gives the formula mass.

Gram Ion (For Ionic species)

The ionic mass of an ionic species expressed in grams is called one gram ion or one gram mole or simply a mole of that ion.

Formula:

$$\text{Number of gram ions or moles of an ionic species} = \frac{\text{Mass of ionic species in grams}}{\text{Formula mass of an ionic specie}}$$

Examples:

1 gram ion of OH^- = 17 g
1 gram ion of CO_3^{2-} = 60 g
1 gram ion of SO_4^{2-} = 96 g

Example 6:

Calculate the gram atoms (moles) in
(a) 0.1 g of sodium.
(b) 0.1 kg of silicon.

Solution:

(a) 0.1 g of sodium

→ Number of gram atoms $= \frac{\text{Given mass (in grams)}}{\text{Molar mass}}$

Mass of sodium = 0.1 g
Molar mass of sodium = 23 g mol^{-1}

→ Number of gram atoms of Na $= \frac{0.1}{23} = 0.0043$ moles $= \boxed{4.3 \times 10^{-3}\ \text{moles}}$

(b) 0.1 kg of Silicon.

→ Mass of silicon = 0.1 kg = 0.1 × 1000g = 100g
Molar mass of silicon = 28.086 g mol^{-1}

→ Number of gram atoms $= \frac{\text{Given mass (in grams)}}{\text{Molar mass}}$

Number of gram atoms of Si $= \frac{100}{28.086} = \boxed{3.56\ \text{moles}}$

Example 7:

Calculate the mass of 10^{-3} moles of $MgSO_4$

Solution:

→ Molar mass of $MgSO_4$ $= 24\times1 + 32\times1 + 16\times4 = 120$ g / mol

Moles of $MgSO_4$ $= 10^{-3}$ moles

→ Number of moles of ionic substance $= \dfrac{\text{Given mass (in grams)}}{\text{Molar mass}}$

Thus $10^{-3} = \dfrac{\text{Given mass (in grams)}}{120}$

Mass $= 120 \times 10^{-3} = \boxed{0.12\ g}$

Exercise Q9:

Define the following terms and give three example of each (vi) Avogadro's number

Avogadro's No

It is the number of particles (atoms, ions, molecules, formula units) present in one mole of a substance.

Its value is 6.02×10^{23}

It is denoted by N_A

Examples:

12 g of C $= 6.02 \times 10^{23}$ atoms of C $= 1$ mole of C

1.008 g of H $= 6.02 \times 10^{23}$ atoms of H $= 1$ mole of H

18 g of H_2O $= 6.02 \times 10^{23}$ molecules of H_2O $= 1$ mole of H_2O

58.5 g of NaCl $= 6.02\times10^{23}$ formula units of NaCl $= 1$ mole of NaCl

One mole of different substances has different masses but same number of particles.

It is because individual particles of different substances have different masses, therefore, equal number of moles of different substances will also have different masses but same number of particles.

- An atom of sodium is 23 times heavier than one atom of hydrogen. Thus in order to have same number of atoms, Na must be taken 23 times greater in mass than hydrogen.
- Similarly, Mg atom is twice heavier than C. Thus, 10 g of Mg and 5 g of C have same number of atoms.

Formulas to calculate the number of particles

Number of atoms, ions or molecules can be calculated by using following formulas.

$$\text{Number of atoms of an element} = \frac{\text{mass of the element}}{\text{atomic mass}} \times N_A$$

$$\text{Number of molecules of a compound} = \frac{\text{mass of the compound}}{\text{molecular mass}} \times N_A$$

$$\text{Number of ions of an ionic specie} = \frac{\text{mass of the ion}}{\text{ionic mass}} \times N_A$$

Simple Quick Calculation Examples to Understand Mole and Avogadro's Number

Example 1:

- One mole water (H_2O) = 18 g = 6.02×10^{23} molecules.

  Thus, one mole of water contains $2\times6.02\times10^{23}$ atoms of hydrogen and 6.02×10^{23} atoms of oxygen.
- One mole of H_2SO_4 = 98g = 6.02×10^{23} molecules.

  Thus one mole of H_2SO_4 contains $2\times6.02\times10^{23}$ atoms of hydrogen, 6.02×10^{23} atoms of sulphur and $4\times6.02\times10^{23}$ atoms of oxygen.

Example 2:

Some substances ionize in water. Their number of positive and negative ions can be calculated.

Let 9.8 g of H_2SO_4 has been dissolved in water.

Number of moles of H_2SO_4 = 9.8 / 98g = 0.1 moles of H_2SO_4

H_2SO_4 ionizes in water completely.

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

Since, 1 mole of H_2SO_4 gives 2 moles of H^+ ions, 1 mole of SO_4^{2-} ions, 2 moles of positive charges *(two H^+ ions, since each H^+ ion has one positive charge)* and 2 moles of negative charges *(one SO_4^{2-} ions, since each SO_4^{2-} has two negative charges)*

So, ***0.1 mole of H_2SO_4 gives 0.2 moles of H^+ ions, 0.1 mole of SO_4^{2-} ions, 0.2 moles of positive charges and 0.2 moles of negative charges.***

Thus, Number of positive ions (H^+ ions) $= 0.2\times6.02\times10^{23}$ ions

Number of negative ions (SO_4^{2-} ions) $= 0.1\times6.02\times10^{23}$ ions

So, Total positive charges $= 0.2\times6.02\times10^{23}$

Total negative charges $= 0.2\times6.02\times10^{23}$.

Total mass of H^+ ions $= (0.2\times1.008)$g

Total mass of SO_4^{2-} ions $= (0.1 \times 96)$g

Example 8:

How many molecules of water are there in 10.0 g of ice? Also calculate the number of atoms of hydrogen and oxygen separately, the total number of atoms and the covalent bonds present in the sample. *(Gujranwala Board, 2010, Lahore Board, 2013)*

Solution:

- Mass of ice (water) $= 10\ g$
  Molar mass of water $= 18\ g/mol$
- Number of molecules of water $= \dfrac{\text{Given Mass (in grams)}}{\text{molar mass}} \times N_A$

Number of molecules of water $= \dfrac{10}{18} \times 6.02 \times 10^{23} = \boxed{3.34 \times 10^{23}\ \text{molecules}}$

- 1 molecule of water contains H atoms $= 2$
  3.34×10^{23} molecules of water contain H atoms $= 2 \times 3.34 \times 10^{23}$
  $= \boxed{6.68 \times 10^{23}\ \text{atoms}}$
- 1 molecule of water contains O atoms $= 1$
  3.34×10^{23} molecules of water contain O atoms $= 3.34 \times 10^{23}$ atoms
  Total number of atoms of H and O $= 6.68 \times 10^{23} + 3.34 \times 10^{23}$
  $= \boxed{10.02 \times 10^{23}\ \text{atoms}}$

1 molecule of water contain number of covalent bonds $= 2$
3.34×10^{23} molecules of water contain $= 2 \times 3.34 \times 10^{23}$
$= \boxed{6.68 \times 10^{23}\ \text{covalent bonds}}$

Example 9:

10.0 g of H_3PO_4 have been dissolved in excess of water to dissociate it completely into ions. Calculate,

(a) Number of molecules in 10.0 g of H_3PO_4.

(b) Number of positive and negative ions in case of complete dissociation in water. (What is the number of H^+ ions in 9.8 g of H_3PO_4? (Faisalabad Board, 2009)

(c) Masses of individual ions.

(d) Number of positive and negative charge dispersed in the solution.

Solution:

(a) Number of molecules in 10.0 g of H_3PO_4

→ Mass of $H_3PO_4 = 10g$
Molar mass of $H_3PO_4 = 3 + 31 + 64 = 98\ g/mol$

→ Number of molecules $= \dfrac{\text{Given mass (in grams)}}{\text{Molar mass}} \times N_A$

Number of molecules of $H_3PO_4 = \dfrac{10}{98} \times 6.02 \times 10^{23}$
$= 0.614 \times 10^{23}$ molecules
$= \boxed{6.14 \times 10^{22}\ \text{molecules}}$

(b) Number of positive and negative ions in case of complete dissociation in water

→ H_3PO_4 ionizes in water as follows

$$H_3PO_4 \longrightarrow 3H^+ + PO_4^{3-}$$

→ According to the balanced equation
1 molecule of H_3PO_4 produces H^+ ions $= 3$
6.14×10^{22} molecules produce H^+ ions $= 3 \times 6.14 \times 10^{22}$
$= \boxed{1.842 \times 10^{23}\ \text{ions}}$

→ According to the balanced equation
1 molecule of H_3PO_4 produces PO_4^{3-} ions $= 1$
6.14×10^{22} molecules produce PO_4^{3-} ions $= 1 \times 6.14 \times 10^{22}$
$= \boxed{6.14 \times 10^{22}\ \text{ions}}$

(c) Masses of individual ions

→ Since Number of ions $= \dfrac{\text{Mass of the ion}}{\text{Ionic mass of the ion}} \times N_A$

Thus Number of H^+ ions $= \dfrac{\text{Mass of the } H^+ \text{ ions}}{\text{Ionic mass of } H^+ \text{ ions}} \times N_A$ **Ionic Mass of H^+ ion = 1.008 g**

$1.842 \times 10^{23} = \dfrac{\text{Mass of the } H^+ \text{ ions}}{1.008} \times 6.02 \times 10^{23}$

Mass of the H^+ ions $= \dfrac{1.842 \times 10^{23}}{6.02 \times 10^{23}} \times 1.008$

Mass of the H^+ ions $= \boxed{0.308\ g}$

Ionic Mass of PO_4^{3-} ion = 95 g

→ and Number of PO_4^{3-} ions $= \dfrac{\text{Mass of the } PO_4^{3-} \text{ ions}}{\text{Ionic mass of } PO_4^{3-} \text{ ions}} \times N_A$

$6.14 \times 10^{22} = \dfrac{\text{Mass of the } PO_4^{3-} \text{ ions}}{95} \times 6.02 \times 10^{23}$

Mass of the PO_4^{3-} ions $= \dfrac{6.14 \times 10^{22}}{6.02 \times 10^{23}} \times 95$
$= \boxed{9.689\ g}$

(d) Number of positive and negative charges dispersed in the solution

- 1 molecule of H_3PO_4 produces positive charges $= 3$
  6.14×10^{22} molecules of H_3PO_4 will gives $= 3 \times 6.14 \times 10^{22}$
  $= \boxed{1.842 \times 10^{23}}$ positive charges
- Since Numbers of positive and negative charges are always equal.

So the number of negative charges produced in the solution = $\boxed{1.842 \times 10^{23}}$

Standard Temperature and Pressure

Gas volumes are usually compared at 0°C (273K) and 1 atm. These conditions are called as standard temperature and pressure (STP).

Exercise Q9:
Define the following terms and give three example of each. (v) Molar Volume

Molar Volume

The volume occupied by one mole of an ideal gas at standard temperature and pressure (S.T.P.) is called molar volume and is equal to 22.414 dm³.

The molar volume for real gases used for calculations is also 22.414 dm^3.

One mole of any gas contains constant number of molecules. This number is called Avogadro's number. Its value is 6.02×10^{23}.

Examples

1 mole of H_2 = 6.02×10^{23} molecules of H_2 = 2.016 g of H_2 = 22.414 dm^3 of H_2 at S.T.P.
1 mole of CH_4 = 6.02×10^{23} molecules of CH_4 = 16 g of CH_4 = 22.414 dm^3 of CH_4 at S.T.P.
1 mole of O_2 = 6.02×10^{23} molecules of O_2 = 32 g of O_2 = 22.414 dm^3 of O_2 at S.T.P.

22.414 dm³ of each gas has different masses but same number of molecules.

It is because masses and sizes of molecules has no effect on volume of gases. In gases molecules are widely separated from one another and have large empty spaces. The distance between two molecules is approximately 300 times of the diameter of the molecules.

Example 10:
A well known ideal gas is enclosed in a container having volume 500 cm³ at S.T.P. Its mass comes out to be 0.72g. What is the molar mass of this gas.

Solution:

→ Volume of an ideal gas at STP = 500 cm^3
Mass of ideal gas = 0.72 g
Molar mass of gas = ?

→ 22.414 dm^3 or 22414 cm^3 of the ideal gas at S.T.P = 1 mole

$$500\ cm^3 \text{ of the ideal gas at S.T.P} = \frac{1 \times 500}{22414} = 0.0223 \text{ moles}$$

→ Since
$$\text{Number of moles} = \frac{\text{Given mass (in grams)}}{\text{Molar mass}}$$

$$0.0223 = \frac{0.72}{\text{Molar mass}}$$

$$\text{Molar mass} = \frac{0.72}{0.0223} = \boxed{32\ g/mol}$$

STOICHIOMETRY

Exercise Q9:
Define the following terms and give three example of each. (vii) Stoichiometry
Exercise: Q.23. (a)
What is stoichiometery? Give its assumptions. Mention two important laws, which help to perform the stoichiometric calculations.

Definition: The branch of chemistry which deals with the study of relationship between the quantities of reactants and products as given by balanced chemical equation is called stoichiometry.

Stoichiometric Assumptions

The stoichiometric calculations are based on following assumptions.
(i) Reactants are completely converted into products.
(ii) No side reaction occurs.

Laws to be obeyed in Stoichiometry

For calculations, the law of conservation of mass and the law of definite proportions are obeyed.

(i) **Law of Conservation of Mass**

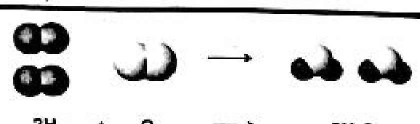
It states

Mass can neither be created nor destroyed during a chemical reaction.

It can also be stated as

Total mass of reactants is equal to the total mass of products.

Thus total number of atoms entering into a chemical reaction is equal to the total number of atoms in the products.

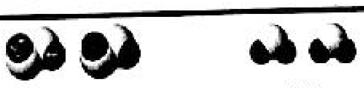


$2H_2$ + O_2 ⟶ $2H_2O$

(ii) Law of Definite Proportions

It states

A pure chemical compound always contains the same elements combined in the same ratio by weight.



H_2O_2 H_2O

Stoichiometric Relationships

Mass-Mass Relationship

With the help of mass of given substance, mass of another substance can be calculated.

Mass-Mole Relationship

With the help of mass of one substance, moles of other substance can be calculated and vice versa.

Mass-Volume Relationship

With the help of mass of one substance volume of the other substance can be calculated and vice versa.

Mole-Mole Relationship

With the help of moles of a given substance, moles of another substance can be calculated.

Advantages and Limitations of Chemical Equations

Advantage

Consider the reaction

$C + O_2 \rightarrow CO_2$

This equation tells that 1 mole of C, reacts with 1 mole of O_2 give one mole of CO_2. Thus, this equation can be used to study quantitative relationship between reactants and products.

Limitations

Chemical equations have certain limitations.

(i) These cannot tell about the conditions of reactions.

(ii) These cannot tell about the rate of reactions.

(iii) These cannot tell about the time to complete the reaction.

(iii) These can also be written for such reactions, which are not possible.

Stoichiometric amounts

The amount of reactants according to balanced chemical equation are called stoichiometric amounts.

Example:

$C + O_2 \rightarrow CO_2$

This equation tells that 1 mole of C reacts with 1 mole of O_2. So, C to O_2 mole ratio is 1:1. Any amount which is according to this ratio will be stoichiometric amount. **e.g.** (12g C and 32g O_2), (24g C and 64g O_2) and (48g C and 128g O_2) are all stoichiometric amounts.

Example 11:

Calculate the number of grams of K_2SO_4 and water produced when 14 g of KOH are reacted with excess of H_2SO_4. Also calculate the number of molecules of water produced.

*(D.G. Khan Board, **2011**: Lahore Board, **2011**: Multan Board, **2010**: Sargodha Board, **2010**)*

Solution:

→ The balanced chemical equation for the chemical reaction is

$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$

→ Given Mass of KOH $= 14\ g$

Molar mass of KOH $= 39 + 16 + 1 = 56\ g/mol$

$$\text{Moles of KOH} = \frac{14}{56} = 0.25 \text{ moles}$$

→ According to balanced chemical equation

Compare the moles of KOH and K_2SO_4

	KOH	:	K_2SO_4
	2 moles	:	1 mole
Therefore	0.25 moles :		$\frac{1 \times 0.25}{2} = 0.125$ moles

No. of moles of K_2SO_4 produced = 0.125 moles

Molar mass of K_2SO_4 $= 2 \times 39 + 32 + 4 \times 16$

$= 174\ g/mol$

Thus Mass of K_2SO_4 produced = No. of moles × Molar mass

$= 0.125 \times 174$

$= \boxed{21.75\ g}$

→ For H_2O, compare KOH and H_2O according to the balanced equation.

KOH	:	H_2O
2 moles	:	2

Therefore 0.25 moles : $\frac{2 \times 0.25}{2} = 0.25$ moles

So, the number of moles of water produced $= 0.25$ moles

Thus Mass of H_2O produced $=$ No. of moles × Molar mass

$= 0.25 \times 18 = \boxed{4.5\ g}$

→ Since Number of molecules $= \frac{\text{Given mass (in grams)}}{\text{Molar mass}} \times N_A$

Therefore Number of water molecules $= \frac{4.5}{18} \times 6.02 \times 10^{23}$

$= \boxed{1.505 \times 10^{23} \text{ molecules}}$

Example 12:

Mg metal reacts with HCl to give hydrogen gas. What is the minimum volume of HCl solution (27% by weight) required to produce 12.1 g of H_2. The density of HCl solution 1.14 g/cm^3 *(Lahore Board, 2007, 2010)*

Solution

→ The balanced chemical equation for the chemical reaction is

$$Mg + 2HCl \longrightarrow MgCl_2 + H_2$$

→ Mass of H_2 produced $= 12.1$ g

Molar mass of $H_2 = 2.016$ g / mol

$$\text{Moles of } H_2 = \frac{12.1}{2.016} = 6 \text{ moles}$$

→ Compare H_2 and HCl according to balance equation.

	H_2	:	HCl
	1 mole	:	2
Therefore	6 moles	:	$6 \times 2 = 12$ moles

Hence Mass of HCl = Moles of HCl × Molar mass of HCl

$= 12 \times 36.5$

$= 438$ g

→ Since solution of HCl is 27% by weight, therefore

27 g of HCl are present in HCl solution $= 100$ g

438 g are present in HCl solution $= \frac{100 \times 438}{27}$

$= 1622.2$ g

→ Density of HCl solution $= 1.14$ g/cm^3

Mass of HCl solution $= 1622.4$ g

Since $d = \frac{m}{V}$

or $V = \frac{m}{d} = \frac{1622.4}{1.14} = \boxed{1423 \text{ cm}^3}$

LIMITING REACTANT

Exercise Q23 (b):

What is limiting reactant? How does it control the quantity of the product formed? Explain with three examples.

Definition:

(i) The reactant which consumes first in the chemical reaction is called limiting reactant.

(ii) The reactant which controls the amount of product formed during a chemical reaction is called limiting reactant.

(iii) The reactant, which gives least amount of product, is the limiting reactant.

Explanation:

When the reactants are not mixed in stoichiometric amounts, one of the reactants is consumed earlier. This is the limiting reactant. Other reactants are left unreacted.

When the limiting reactant is consumed, then reaction stops and further product cannot be produced. Thus, it controls the amount of product and gives the least amount of product.

Example 1:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

When 2 moles of hydrogen (4g) reacts with 2 moles of oxygen (64g), then only 2 moles (36g) of water are produced. It is because, 2 moles (4g) of hydrogen react with 1 mole (32g) of oxygen. Since, less hydrogen is present than oxygen, so hydrogen is the limiting reactant.

Example 2:

Burning of coal occurs in excess of oxygen. In this coal is the limiting reactant while oxygen is in excess.

Example 3:

Rusting of iron occurs in excess of oxygen present in air. In this, iron is the limiting reactant while oxygen is in excess.

Application of Deliberate use of Limiting reactant

Example 1: To completely consume the expensive reactant

The other reactants are taken in large excess than expensive reactants. It ensures that all of the expensive reactant is completely used up in the chemical reaction, so it becomes the limiting reactant.

Example 2: To speed up the reaction.

Rate of reaction is directly proportional to the amounts of reactants. So, a large quantity of one reactant may speed up the reaction. e.g. a large quantity of oxygen burns things faster. Thus excess of oxygen is left behind at the end of reaction and burning things like paper, wood etc. are the limiting reactants.

Determination of Limiting Reactant

The amount of product formed by a chemical reaction is calculated from the limiting reactant; therefore, identification of limiting reactant is necessary.

Following procedure is used for this

(i) Number of moles of each reactant is calculated from given masses.

(ii) Using balanced chemical equation, amount of product, expected to form, from each reactant is calculated.

(iii) The reactant, which gives least amount of product, is the limiting reactant.

Example 13:

NH_3 gas can be prepared by heating together two solids NH_4Cl and $Ca(OH)_2$. If a mixture containing 100 g of each solid is heated then

(a) Calculate the number of grams of NH_3 produced.

(b) Calculate the excess amount of reagent left unreacted.

(Faisalabad Board, **2010**: Gujranwala Board, **2011**: Multan Board, **2013**: Sargodha Board, **2011, 2013**)

Solution:

→ The balanced chemical equation for the chemical reaction is

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$$

(a) Number of grams of NH_3 produced.

→ Given Mass of NH_4Cl = 100g

Molar mass of NH_4Cl = $14+1\times4+35.5 = 53.5\ g/mol$

$$\text{Number of moles of } NH_4Cl = \frac{100}{53.5} = 1.87\text{moles}$$

Given Mass of $Ca(OH)_2$ = 100 g

Molar mass of $Ca(OH)_2$ = $40+2(16+1)=74\ g$

$$\text{Number of moles of } Ca(OH)_2 = \frac{100}{74} = 1.35 \text{ moles}$$

→ Compare NH_4Cl and NH_3 according to balanced chemical equation.

	NH_4Cl	:	NH_3
	2 moles	:	2 moles
Therefore	1.87 moles	:	$\frac{2}{2}\times1.87 = 1.87$ moles

Compare $Ca(OH)_2$ and NH_3 according to balanced chemical equation.

	$Ca(OH)_2$	:	NH_3
	1 mole	:	2 moles
Therefore	1.35 moles	:	$2\times1.35 = 2.70$ moles

→ Since NH_4Cl produces least amount of NH_3, hence NH_4Cl is the limiting reactant.

Thus no. of moles of NH_3 produced = 1.87 moles

Molar mass of NH_3 = $14+1\times3=17\ g/mol$

Hence Amount of NH_3 produced = No. of moles × Molar Mass of NH_3

$= 1.87\times17$

$= \boxed{31.79\ g}$

(b) Amount of reagent left unreacted.

→ Compare NH_4Cl and $Ca(OH)_2$ according to balanced chemical equation.

NH_4Cl	:	$Ca(OH)_2$
2 moles	:	1 moles
1.87 moles	:	$\frac{1\times1.87}{2} = 0.935$ moles

→ Moles of $Ca(OH)_2$ taken = 1.35 moles

Therefore unreacted moles = $1.35 - 0.935$ = 0.415 moles

Molar Mass of $Ca(OH)_2$ = 74 g/mol

Thus Mass of $Ca(OH)_2$ left = $0.415\times74 = \boxed{30.71\ g}$

Exercise Q9:

Define the following terms and give three example of each. (viii)Percentage yield

Exercise Q.24.(a):

Define yield. How do we calculate the yield of a chemical reaction?

YIELD

The amount of product formed during a chemical reaction is called Yield.

Theoretical Yield

The amount of product calculated from balanced chemical equation is called theoretical yield

It is the maximum yield of product that can be produced by a given amount of reactant according to balanced chemical equation.

Example:

H_2 & O_2 react together as

$$2H_2 + O_2 \longrightarrow 2H_2O$$

According to this equation 2 moles of H_2 & 1 mole of O_2 should form 2 moles of H_2O. Therefore, 2 moles of H_2O is the theoretical yield.

Actual Yield

The amount of product actually obtained during a chemical reaction is called Actual yield.

Percentage Yield (or Efficiency of a Reaction)

The % yield or efficiency of the reaction is given by the formula

% Yield = [illegible]

Exercise Q24 (b):

What are the factors, which are mostly responsible for the low yield of products in chemical reaction?

Actual yield of a chemical reaction is always less than its theoretical yield.

The reasons are

(i) Inexperience worker wastes a significant amount of product.

(ii) By product may be formed due to side reactions.

(iii) The reversible reactions are never completed.

(iv) Product is lost during their separation and purification processes. e.g. processes like filtration, distillation, separation by separating funnel, washing, drying and crystallization reduces the amount of product.

Difference between Actual Yield and Theoretical Yield

	Actual Yield		Theoretical Yield
1	It is the amount of a product actually obtained during a chemical reaction.	1	It is the amount of a product calculated from a balanced chemical equation.
2	It is always less than the theoretical yield.	2	It is always greater than actual yield.
3	Reversible nature of the reaction and side reactions decreases the actual yield.	3	While calculating theoretical yield, it is assumed that (i) No side reaction occurs (ii) Reactants are completely converted into products. Therefore, it is not decreased
4	Loss of product during separation, purification and by inexperience worker decreases the yield.	4	No mechanical losses occur, since it is calculated theoretically.
5	It is an experimental term.	5	It is a theoretical term.

Example 14:

When lime stone ($CaCO_3$) is roasted, quicklime (CaO) is produced according to the following equation. The actual yield of CaO is 2.5 kg, when 4.5 kg of lime stone is roasted. What is the percentage yield of this reaction?

(Faisalabad Board, 2013: Multan Board, 2010: Rawalpindi Board, 2013)

Solution:

→ The balanced chemical equation for the chemical reaction is

$$CaCO_3 \longrightarrow CaO + CO_2$$

→ Mass of lime stone = 4.5 kg = 4500 g

Molar mass of $CaCO_3$ = 100 g/mol

Moles of $CaCO_3$ = 4500 / 100 = 45 moles

→ Mass of quick lime produced = 2.5 kg = 2500 g ***(actual yield)***

→ According to the balanced chemical equation

Compare the moles of $CaCO_3$ and CaO

	$CaCO_3$	:	CaO
	1 mole	:	1 mole
Therefore	45 moles	:	1 × 45 = 45 moles

Molar mass of CaO $= 40+16 = 56$ g/mol

Thus

Mass of CaO produced $= 45 \times 56 = 2520$ g

→ Hence Theoretical yield of CaO $= 2520$ g

Actual yield of CaO $= 2500$ g

% yield is given by

$$\%\ \text{yield} = \frac{\text{Actual yield}}{\text{Theoretical yeild}} \times 100$$

$$= \frac{2500}{2520} \times 100$$

$$= \boxed{99.2\%}$$

OBJECTIVE AND SHORT ANSWER QUESTIONS (Exercise)

Q.1. *Select the most suitable answer from the given ones in each question*

(i) Isotopes differ in

(a) properties which depend upon mass
(b) arrangement of electrons in orbital
(c) chemical properties
(d) the extent to which they may be affected in electromagnetic field

(Faisalabad Board, 2009, 2011: D.G. Khan Board, 2009: Faisalabad Board, 2011: D.G. Khan Board, 2012)

(ii) Which of the following statement is not true? *(Lahore board, 2015)*

(a) Isotopes with even atomic masses are comparatively abundant
(b) Isotopes with odd atomic masses are comparatively abundant.
(c) Isotopes with even atomic masses and even atomic numbers are comparatively abundant.
(d) Isotopes with even atomic masses and odd atomic numbers are comparatively abundant.

(iii) Many elements have fractional atomic masses, this is because

(a) the mass of the atom is itself fractional
(b) atomic masses are average masses of isobars
(c) atomic masses are average masses of isotopes
(d) atomic masses are average masses of isotopes proportional to their relative abundance.

(iv) The mass of one mole of electrons is

(a) 1.008mg (b) 0.55mg (c) 0.184mg (d) 1.673mg

(Faisalabad Board, 2007, 2009: Multan Board, 2011, 2012: Sargodha Board, 2012, 2014: Gujranwala Board, 2010, 2012, 2013: Lahore Board, 2014)

(v) 27 g of Al will react completely with how much mass of O_2 to produce Al_2O_3

(a) 8g of oxygen (b) 16g of oxygen (c) 32g of oxygen (d) 24g of oxygen

(Multan Board, 2010: Rawalpindi Board, 2010, 2012: D.G. Khan Board, 2012: Sargodha Board, 2013: Lahore board, 2013)

(vi) The number of moles of CO_2 which contain 8 g of oxygen

(a) 0.25 (b) 0.50 (c) 1 (d) 1.5

(Rawalpindi Board, 2009: Gujranwala board, 2009, 2012, 2014: Multan Board, 2013)

(vii) The largest number of molecules is present in

(a) 3.6g of H_2O (b) 4.8g of C_2H_5OH (c) 2.8g of CO (d) 5.4g of N_2O_5

(Multan Board, 2008: D.G. Khan Board, 2009: Sargodha Board, 2011, 2012: Rawalpindi Board, 2011: Rawalpindi Board, 2012: Multan Board, 2011: Lahore Board, 2014)

(viii) One mole of SO_2 contains

(a) 6.02×10^{23} atoms of oxygen (b) 1.81×10^{23} molecules of SO_2
(c) 6.02×10^{23} atoms of sulphur (d) 4g atom of SO_2

(Bahawalpur Board, 2009: Sargodha Board, 2009: Gujranwala Board, 2013: Multan Board, 2012)

(ix) The volume occupied by 1.4g of N_2 at STP is

(a) $2.24dm^3$ (b) $22.4dm^3$ (c) $1.12dm^3$ (d) $112cm^3$

(Gujranwala board, 2008, 2014: Sargodha Board, 2009, 2011: Lahore Board, 2010)

(x) A limiting reactant is the one which

(a) is taken in lesser quantity in grams as compared to other reactants

(b) is taken in lesser quantity in volume as compared to the other

(c) carries the maximum amount of the product which is required

(d) gives the minimum amount of the product under consideration

(Gujranwala board, 2009: Multan Board, 2010: Bahawalpur Board, 2010)

ANSWERS TO MULTIPLE CHOICE QUESTIONS	
(i) Ans (a) Isotopes have same atomic number but <u>different atomic masses.</u>	**(ii) Ans (d)** <u>Isotopes with odd atomic masses are comparatively less abundant.</u> Isotopes with even atomic number and even mass are more abundant. Out of <u>280 natural isotopes</u>, <u>154</u> have <u>even</u> mass number and <u>even</u> atomic number
(iii) Ans (d) The atomic masses of elements are calculated from their <u>number</u> of isotopes and their <u>natural abundance</u>. Since the calculated masses are average masses, therefore, many elements have fractional atomic masses.	**(iv) Ans (b)** 1 mole of electrons = 6.02×10^{23} electrons 1 electron has mass = 9.1×10^{-31} kg 6.02×10^{23} electron has mass = $9.1 \times 10^{-31} \times 6.02 \times 10^{23}$ $= 5.5 \times 10^{-7}$ kg Since 1 kg = 10^6 mg, therefore Mass of 1 mole of electron = 5.5×10^{-7} kg $\times 10^6$ = 0.55 mg
(v) Ans (d) Moles of Al = $\frac{27}{27}$ = 1 mole According to balanced eq. $4Al + 3O_2 \longrightarrow 2Al_2O_3$ Al : O_2 4 : 3 1 : ¾ moles Mass of O_2 = $\frac{3}{4} \times 32 = 24$ g	**(vi) Ans (a)** 32 g. of O are present in CO_2 = 1 mole 8 g. of O are present in CO_2 = $\frac{1 \times 8}{32}$ = 0.25 mole
(vii) Ans (a) No. of molecules of H_2O $= \frac{3.6}{18} \times 6.02 \times 10^{23}$ $= 0.2 \times N_A$ No. of molecules of $C_2H_5OH = \frac{4.6}{46} \times 6.02 \times 10^{23}$ $= 0.1 \times N_A$ No. of molecules of CO $= \frac{2.8}{28} \times 6.02 \times 10^{23}$ $= 0.1 \times N_A$ No. of molecules of N_2O_5 $= \frac{5.4}{108} \times 6.02 \times 10^{23}$ $= 0.05 \times N_A$	**(viii) Ans (b)** One mole of SO_2 contains: • One mole of Sulphur atoms, and • Two moles of oxygen atoms. Thus, No. of sulphur atoms = $1 \times 6.02 \times 10^{23}$ and No. of Oxygen atoms = $2 \times 6.02 \times 10^{23}$
(ix) Ans (a) Moles of N_2 = $\frac{1.4}{28}$ = 0.05 mole 1 mole of N_2 at S.T.P. occupies vol. = 22.414 dm^3 0.05 mole N_2 at S.T.P. occupies vol = 22.414 x 0.05 = 1.12 dm^3	**(x) Ans (d)** The reactant which gives minimum amount of product is called limiting reactant.

Q.2. Fill in the blanks

(i) The unit of relative atomic mass is expressed in _______.

(ii) The exact masses of isotopes can be determined by _______.

(iii) The phenomenon of isotopy was first discovered by _______.

(iv) Empirical formula can be determined by combustion analysis for those compounds which have _____ and _____ in them.

(v) A limiting reagent is that which controls the quantities of _____.

(vi) 1 mole of glucose has ______ atoms of carbon, _____ of oxygen and _____ of hydrogen.

(vii) 4 g of CH_4 at 0^oC and 1 atm pressure has _____ molecules of CH_4.

(viii) Stoichiometric calculations can be performed only when _______ is obeyed.

Answers:
(i) amu (ii) mass spectrometry (iii) Soddy (iv) carbon, hydrogen
(v) product (vi) 6 N_A, 12 N_A, 6 N_A (vii) 1.505×10^{23}
(viii) law of conservation of mass

Q.3. Indicate the true or false as the case may be

(i) Neon has three isotopes and the fourth one with atomic mass 20.18 amu.

(ii) Empirical formula gives the information about the total number of atoms present in the molecule.

(iii) During combustion analysis $Mg(ClO_4)_2$ is employed to absorb water vapours.

(iv) Molecular formula is the integral multiple of empirical formula and the integral multiple can never be unity.

(v) The number of atoms in 1.79g of gold and 0.023g of sodium are equal.

(vi) The number of electrons in the molecules of CO and N_2 are 14 each, so 1 mg of each gas will have same number of electrons.

(vii) Avogadro's hypothesis is applicable to all types of gases i.e. ideal and non-ideal.

(viii) Actual yield of a chemical reaction may be greater than the theoretical yield.

Answers:
(i) False (ii) False (iii) True (iv) False (v) False
(vi) True (vii) False (viii) False

Q4. What are ions? under what conditions are they produced?

Ions are those species which carry either positive or negative charge.

These may be produced

(i) <u>Positive ions are produced by</u> passing <u>high energy electron beam</u>, <u>α-particles</u> or <u>X-rays</u> through a gas.

e.g. $Na \rightarrow Na^+ + e^-$

(ii) Negative ions are produced by the addition of an electron to a neutral species.

e.g. $Cl + e^- \rightarrow Cl^-$

(iii) By ionization of an ionic compound in water.

e.g. $NaCl \rightleftharpoons Na^+ + Cl^-$

Q5.(a) What are the isotopes? How do you deduce the fractional atomic masses of elements from the relative isotopic abundances? Give two examples in the support of your answer?

Solved on Page

(b) How does a mass spectrograph show the relative abundance of isotopes of an element

Solved on Page 12

(c) What is the justification of two strong peaks in the mass spectrum of bromine, while for iodine only one peak at 127 a.m.u. is indicated?

- Bromine has two naturally occurring isotopes with almost equal relative abundance, therefore, its mass spectrum shows two strong peaks.
- While iodine has only one naturally occurring isotope, therefore, its spectrum shows only one peak.

Q9. Define the following terms and give three example of each.

(i) Gram atom: *Solved on page 20*	(ii) Gram molecular mass: *Solved on page 20*
(ii) Gram formula: *Solved on page 20*	(iv) Gram ion: *Solved on page 21*
(v) Molar Volume: *Solved on page 26*	(vi) Avogadro's number: *Solved on page 22*
(vii) Stoichiometry: *Solved on page 27*	(viii) Percentage yield: *Solved on page 34*

Q9. Justify the following statement:

(a) 23 gram of sodium and 238 grams of uranium have equal number of atoms in them. *(Faisalabad Board, 2007: Lahore Board, 2006: Multan Board, 2010)*

1 mole of Na = 23 g

1 mole of U = 238 g

Since 1 mole of each element contains Avogadro's number of atoms and there is 1 mole of each of Na and U. Hence 23 g of Na and 238 g of U contains equal number of atoms. i.e. 6.02×10^{23}

(b) Mg atom is twice heavier than that of carbon. *(Gujranwala Board, 2011, 2014), (Lahore Board, 2007, 2011), (Rawalpindi Board, 2008, 2010)*

One atom of carbon contains 6 protons and 6 neutrons in its nucleus and its atomic mass on atomic mass unit scale is 12 amu.

While one atom of Mg contains 12 protons and 12 neutrons in its nucleus and its atomic mass on atomic mass unit scale is 24 amu. Thus, $\frac{24\ amu}{12\ amu} = 2$. Hence, one atom of Mg is twice heavier than that of one atom of carbon.

(c) 180g of glucose and 342g of sucrose have same number of molecules but different number of atoms. *(Gujranwala Board, 2012: Lahore Board, 2006: Sargodha Board, 2012)*

180 g of glucose = 1 mole

342 g of sucrose = 1 mole

1 mole of each compound contains Avogadro's number of molecules. Hence, 180 g of glucose (1 mole) and 342 g (1 mole) of sucrose contain equal number of molecules. i.e. 6.02×10^{23}

Since one molecule of glucose ($C_6H_{12}O_6$) contains 24 atoms. Whereas, one molecule of sucrose ($C_{12}H_{22}O_{11}$) contains 45 atoms, therefore, equal number of molecules of glucose and sucrose will have different number of atoms.

(d) 4.9g of H_2SO_4 when completely ionized in water have equal number of positive and negative charges but the number of positively charge ions are twice the number of negatively charge ions. *(Lahore Board, 2012)*

H_2SO_4 ionizes in solution as

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$

This balanced equation shows that

1 molecule of H_2SO_4 produces

Number of positively charged ions (H^+ ions) = 2

Number of negatively charged ions (SO_4^{2-}) = 1

Number of positive charges = 2 (due to two H^+ ions)

Number of negative charges = 2 (due to two negative charges on SO_4^{2-})

Hence, whatever be the amount of H_2SO_4, it will always produce equal number of positive and negative charges but number of positively charged ions will be twice the number of negatively charged ions.

(e) One mg of $K_2Cr_2O_7$ has thrice the number of ions than the number of molecules when ionized in water. *(Lahore Board, 2010: 2012, 2013)*

$K_2Cr_2O_7$ ionizes as

$$K_2Cr_2O_7 \rightleftharpoons 2K^+ + Cr_2O_7^{2-}$$

This equation shows that 1 formula unit of $K_2Cr_2O_7$ produces two K^+ ions and one $Cr_2O_7^{2-}$ ion in solution. Thus a total of three ions are produced by the ionization of 1 formula unit of $K_2Cr_2O_7$.

Hence whatever be the amount of $K_2Cr_2O_7$, number of ions in its solution will always be thrice than the number of its formula units (molecules).

(f) Two grams of H_2, 16g of CH_4 and 44g of CO_2 occupy separately the volume of 22.414 dm^3, although the size and masses of molecules of these gases are very different from each other. *(Multan Board, 2007)*

2 grams of H_2 = 1 mole = 6.023×10^{23} molecules
16 grams of CH_4 = 1 mole = 6.023×10^{23} molecules
44 grams of CO_2 = 1 mole = 6.023×10^{23} molecules

Since 2 g of H_2, 16 g of CH_4 and 44 g of CO_2 contains equal number of molecules and according to Avogadro's law, equal molecules of all gases at S.T.P. occupy same volume i.e. 22.414 dm^3.

In gases distance between two molecules is approximately 300 times its molecular size. Thus, volume occupied by gas molecules does not depend upon the size or mass of molecules and it only depends upon the number of molecules.

Hence equal molecules of H_2, CH_4 and CO_2 at STP will occupy same volume i.e. 22.414 dm^3.

Q23. (a) What is stoichiometery? Give its assumptions. Mention two important laws, which help to perform the stoichiometric calculations.

Solved on Page 34

(b) What is limiting reactant? How does it control the quantity of the product formed? Explain with three examples.

Solved on Page 31

Q24.(a) Define yield. How do we calculate the yield of a chemical reaction?

Solved on Page 34

(b) What are the factors, which are mostly responsible for the low yield of products in chemical reaction?

Solved on Page 35

Q25. Explain the following with reason.

(i) Law of conservation of mass has to be considered during stoichiometric calculations. *(Faisalabad Board, 2007; Lahore Board, 2013)*

Stoichiometric calculations are done with balanced chemical equations in which it is assumed that matter is neither created nor destroyed during a chemical change. Hence law of conservation of mass has to be considered during stoichiometric calculations, otherwise, with unbalanced equations stoichiometric calculations will not be possible.

(ii) Many chemical reactions taking places in our surrounding involve the limiting reactant.

A limiting reactant is one which has limited quantity and consumes first in a chemical reaction.

There are many chemical reactions in our surroundings which involve limiting reactant

- Petrol burns in excess of oxygen present in air
- Rusting of iron occurs in excess of oxygen present in air.
- Burning of coal occurs in excess of oxygen

In above cases, petrol, iron and coal are limiting reactant while oxygen is in excess.

(iii) No individual neon atom in the sample of the element has a mass of 20.18 amu.
*(Gujranwala Board, **2013**; Lahore Board, **2014**; Multan Board, **2007, 2012**; Sargodha Board, **2013**)*

A sample of neon consists of $^{20}_{10}Ne$, $^{21}_{10}Ne$ and $^{22}_{10}Ne$ in the percentages of 90.92%, 0.26%, 8.82% respectively. The average relative mass of Ne is thus calculated as

$$\text{average atomic mass} = \frac{(20 \times 90.92) + (21 \times 0.26) + (22 \times 8.82)}{100} = 20.18$$

Hence 20.18 amu is the average atomic mass of neon and no individual neon atom in the sample that has a mass of 20.18 amu.

(iv) One mole of H_2SO_4 should completely react with two moles of NaOH. How does Avogadro's number help to explain it *(Rawalpindi Board, 2008, 2009)*

The chemical reaction of H_2SO_4 and NaOH is

$$\underset{\substack{\text{2 formula units} \\ \text{or } 2 \times 6.02 \times 10^{23} \text{ formula units} \\ \text{2 moles}}}{2NaOH} + \underset{\substack{\text{1 molecule} \\ 6.02 \times 10^{23} \text{ molecules} \\ \text{1 mole}}}{H_2SO_4} \rightarrow Na_2SO_4 + H_2O$$

Hence 2 moles of NaOH reacts with 1 mole of H_2SO_4

(v) One mole of H_2O has two moles of bond, three moles of atoms, ten moles of electrons and twenty-eight moles of the total fundamental particles present in it.

Bonds

1 molecule of H_2O contain bonds = 2
6.02×10^{23} molecules contain bonds = $2 \times 6.02 \times 10^{23}$
Thus 1 mole of H_2O contain bonds = 2 moles

Atoms

1 molecule of H_2O contain atoms = 3
6.02×10^{23} molecules contain atoms = $3 \times 6.02 \times 10^{23}$
Thus 1 mole of H_2O contain atoms = 3 moles

Electrons

1 molecule of H_2O contains two H atoms and one O atom.

Since
One O atoms contain electrons = 8
One H atoms contain electrons = 1
Two H atoms contain electrons = 2
Hence 1 molecule of H_2O contain electrons = 2+8=10
6.02×10^{23} molecules contain electrons = $10\times6.02\times10^{23}$
Thus 1 mole of H_2O contain electrons = 10 moles

Total Fundamental Particles

1 molecule of H_2O contains two H atoms and one O atom.

Since
1 O atoms contain electrons=8, Protons=8 and Neutrons=8
Thus
1 O atoms contain total fundamental particles = 8+8+8=24
Since
1 H atoms contain electrons=1, Protons=1 and Neutrons=0
Thus
1 H atoms contain total fundamental particles=1+1+0=2
2 H atoms contain total fundamental particles = 4
Hence
1 molecule of H_2O contain fundamental particles = 24+4=28
6.02×10^{23} molecules contain fundamental particles=$28\times6.02\times10^{23}$
Thus 1 mole of H_2O contain bonds = 28 moles

(vi) N_2 and CO has same number of electrons, protons and neutrons
(D.G. Khan Board, 2009; Faisalabad Board, 2010, 2013; Gujranwala Board, 2008, 2012, 2013, 2014; Multan Board, 2012; Sargodha Board, 2011)

The elements C, N and O are represented as $^{12}_{6}C$, $^{14}_{7}N$ and $^{16}_{8}O$

Thus
1 molecule of N_2 contains electrons =7 + 7 =14 (7 for each N atom)
1 molecule of CO contains electrons =6 + 8 =14 (C=6 , O=8)
similarly
1 molecule of N_2 contains protons = 7 + 7 =14 (7 for each N atom)
1 molecule of CO contains protons =6 + 8 =14 (C=6 , O=8)
and
1 molecule of N_2 contains neutrons =7 + 7 =14 (7 for each N atom)
1 molecule of CO contains neutrons =6 + 8 =14 (C = 6 , O = 8)

IMPORTANT FORMULAS

To find the average atomic mass of an element from masses of its isotopes and their relative abundance

$$\text{average atomic mass} = \frac{\text{mass of } 1^{st} \text{ isotope} \times \% \text{abundance} + \text{mass of } 2^{nd} \text{ isotope} \times \% \text{ abundance} + \text{- - - -}}{100}$$

To find the %age of element in a compound

$$\%\text{age of an element} = \frac{\text{Mass of the element}}{\text{Mass of the compound}} \times 100 \quad \text{(from given masses)}$$

$$\%\text{age of an element} = \frac{\text{Mass of the element}}{\text{Formula Mass of the compound}} \times 100 \quad \text{(from given formula)}$$

To find the Empirical Formula

Elements	[illegible]	No of gram atoms or moles	Atomic Ratio	Empirical Formula
C	$\%\text{age of C} = \frac{\text{Mass of } CO_2}{\text{Mass of organic compound}} \times \frac{12}{44} \times 100$	$\frac{\%\text{age}}{12}$	$\frac{\text{No of g atoms}}{\text{Smallest No of g atoms}}$	
H	$\%\text{age of H} = \frac{\text{Mass of } H_2O}{\text{Mass of organic compound}} \times \frac{2.016}{18} \times 100$	$\frac{\%\text{age}}{1.008}$	$\frac{\text{No of g atoms}}{\text{Smallest No of g atoms}}$	
O	% of oxygen = 100 − (% of carbon + % of hydrogen)	$\frac{\%\text{age}}{16}$	$\frac{\text{No of g atoms}}{\text{Smallest No of g atoms}}$	

NOTE. For other elements more boxes can be made

To find molecular formula from empirical formula

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} \quad \text{Molecular formula} = n\,(\text{empirical formula})$$

To find number of moles or mass or molar mass of a compound

$$\text{Moles} = \frac{\text{Mass}}{\text{Molar Mass}}$$

Molar Mass may be Molecular mass or atomic mass or formula mass or ionic mass

To find the number of particles (atoms, ions, molecules or formula units)

$$\text{No of particles} = \frac{\text{Mass}}{\text{Molar Mass}} \times N_A \quad \text{or} \quad \text{No of particles} = \text{moles} \times N_A$$

Molar Mass may be Molecular mass or atomic mass or formula mass or ionic mass

To find the %age yield or efficiency of the reaction

$$\%\text{ yield} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

NUMERICAL PROBLEMS (Exercise)

Q6. Silver has atomic number 47 and has 16 known isotopes but only two occur naturally i.e. ^{107}Ag and ^{109}Ag. Given the following mass spectrometric data, Calculate the average atomic mass of silver.

Isotopes	Mass (a.m.u.)	Percentage Abundance
^{107}Ag	106.90509	51.84
^{109}Ag	108.90476	48.16

Solution:

→ Average atomic mass $= \dfrac{(106.90509 \times 51.84) + (108.90476 \times 48.16)}{100}$

$= \boxed{107.87 \text{ a.m.u.}}$

Q7. Boron with atomic number 5 has two naturally occurring isotopes. Calculate the percentage abundance of ^{10}B and ^{11}B from the following data]

Average Atomic mass of B = 10.81 amu
Isotopic mass of ^{10}B = 10.0129 amu
Isotopic mass of ^{11}B = 11.0093amu

Solution:

→ Let % abundance of $^{10}B = x$
Then % abundance of $^{11}B = 100 - x$
Thus

→ Average atomic mass $= \dfrac{[10.0129 \times x] + [11.0093 \times (100 - x)]}{100} = 10.81$ amu

or $10.0129x + 1100.93 - 11.0093x = 1081$
or $-0.9964x = 1081 - 1100.93$
$-0.9964x = -19.93$

$x = \dfrac{19.93}{0.9964} = 20.002\%$

→ Hence % abundance of $^{10}B = x = \boxed{20.002\%}$
and % abundance of $^{11}B = 100 - 20.002 = \boxed{79.998\%}$

Q.10. Calculate each of the following quantities.

(a) Mass in grams of 2.74 moles of $KMnO_4$ (Multan Board, 2011, 2012: Sargodha Board, 2010)

→ Moles of $KMnO_4$ = 2.74 mol
Molar Mass of $KMnO_4$ = 39+55+16 x 4 = 158 g mol^{-1}

→ 1 mole of $KMnO_4$ = 158 g.
2.74 oles of $KMnO_4$ = 2.74 × 158 = $\boxed{432.92\ g}$

(b) Moles of O atoms in 9.00g of $Mg(NO_3)_2$ (Sargodha Board, 2013)

→ Mass of $Mg(NO_3)_2$ = 9g
Molar Mass of $Mg(NO_3)_2$ = 24+14 x 2+16 x 6 = 148 g mol^{-1}

→ Number of moles of $Mg(NO_3)_2 = \dfrac{\text{Given mass (in grams)}}{\text{Molar mass}}$

$= \dfrac{9}{148} = 0.0608$ moles

→ 1 mole of $Mg(NO_3)_2$ contains O moles = 6 moles
0.0608 moles of $Mg(NO_3)_2$ contain O moles = 6×0.0608 = $\boxed{0.3648\ moles}$

(c) Number of O atoms in 10.037g of $CuSO_4.5H_2O$

→ Mass of $CuSO_4.5H_2O$ = 10.037 g
Molar Mass of $CuSO_4.5H_2O$ = 63.5+32+1×10+16×9 = 249.5 g mol^{-1}

→ Number of moles of of $CuSO_4.5H_2O = \dfrac{\text{Given Mass}}{\text{Molar Mass}}$

$= \dfrac{10.037}{249.5}$

= 0.04 moles

→ 1 mole of $CuSO_4.5H_2O$ contain oxygen = 9 moles
0.04 moles $CuSO_4.5H_2O$ contain oxygen = 0.04 × 9 = 0.36 moles

→ 1 mole of oxygen atoms = 6.02×10^{23} atoms
0.36 moles of oxygen atoms = $0.36 \times 6.02 \times 10^{23}$ atoms
= $\boxed{2.167 \times 10^{23}\ atoms}$

(d) Mass in kilograms of 2.6×10^{20} molecules of SO_2 (Faisalabad Board, 2010: Gujranwala Board, 2004: Lahore Board, 2014)

→ Number of molecules of SO_2 = 2.6×10^{20}
Molar Mass of SO_2 = 32+16 × 2= 64 g mol^{-1}

→ Number of molecules of $SO_2 = \dfrac{\text{Given mass (in grams)}}{\text{Molar mass}} \times N_A$

$2.6 \times 10^{20} = \dfrac{\text{Mass}}{6.4g} \times 6.02 \times 10^{23}$

Mass $= \dfrac{2.6 \times 10^{20} \times 64}{6.02 \times 10^{23}} = 2.76 \times 10^{-2}$g

→ Mass in kg $= \dfrac{2.76 \times 10^{-2}}{1000} = \boxed{2.76 \times 10^{-5}\ kg}$

(Sargodha Board, 2011)

(e) Moles of Cl atoms in 0.822g $C_2H_4Cl_2$

→ Mass of $C_2H_4Cl_2$ = 0.822 g
Molar Mass of $C_2H_4Cl_2$ = $12 \times 2+1 \times 4+35.5 \times 2$ = 99 g mol^{-1}

→ Number of moles of $C_2H_4Cl_2$ = $\frac{\text{Given mass (in grams)}}{\text{Molar mass}}$

Number of moles of $C_2H_4Cl_2$ = $\frac{0.822}{99} = 8.303 \times 10^{-3}$ moles

→ 1 mole of $C_2H_4Cl_2$ contains Cl atoms = 2 moles
8.303×10^{-3} moles contain Cl atoms = $2 \times 8.303 \times 10^{-3}$
= $\boxed{0.0166 \text{ moles}}$

(f) Mass in grams of 5.136 moles of silver carbonate

→ Moles of Ag_2CO_3 = 5.136 mol
Molar Mass of Ag_2CO_3 = 275.74 g mol^{-1}

→ Number of moles of Ag_2CO_3 = $\frac{\text{Given mass (in grams)}}{\text{Molar mass}}$

$5.136 = \frac{\text{Mass}}{275.74}$

Mass = $5.136 \times 275.74 = \boxed{1416.2\ g}$

(g) Mass in grams of 2.78×10^{21} molecules of CrO_2Cl_2

→ Number of molecules of CrO_2Cl_2 = 2.78×10^{21}
Molar Mass of CrO_2Cl_2 = $52+16 \times 2+2 \times 35.5=155$ g mol^{-1}

→ Number of molecules of CrO_2Cl_2 = $\frac{\text{Given mass (in grams)}}{\text{Molar mass}} \times N_A$

$2.78 \times 10^{21} = \frac{\text{Mass}}{155} \times 6.02 \times 10^{23}$

Mass = $\frac{2.78 \times 10^{21} \times 155}{6.02 \times 10^{23}} = \boxed{0.7158\ g}$

(h) Number of moles and formula units in 100g $KClO_3$

→ Mass of $KClO_3$ = 100 g
Molar Mass Of $KClO_3$ = $39+35.5+16 \times 3=122.5$ g mol^{-1}

→ Number of moles of $KClO_3$ = $\frac{\text{Given Mass (in grams)}}{\text{Molar mass}}$

= $\frac{100}{122.5} = 0.816$ moles

→ Number of formula units = $\frac{\text{Given Mass (in grams)}}{\text{Molar mass}} \times N_A$

= $\frac{100}{122.5} \times 6.02 \times 10^{23}$

= $\boxed{4.91 \times 10^{23} \text{ formula units}}$

(i) Number of K^+ ions ClO_3^{-1} ions, Cl atoms, and O atoms in (h)

→ Formula unit of $KClO_3$ = 4.91×10^{23}

→ 1 formula unit of $KClO_3$ contains K^+ ions = 1
4.91×10^{23} formula units contain K^+ ions = $\boxed{4.91 \times 10^{23} \text{ ions}}$

→ 1 formula unit of $KClO_3$ contains ClO_3^- ions= 1
4.91×10^{23} formula units contain ClO_3^- ions= $\boxed{4.91 \times 10^{23} \text{ ions}}$

→ 1 formula unit of $KClO_3$ contains Cl atoms = 1
4.91×10^{23} formula units contain Cl atoms= $\boxed{4.91 \times 10^{23} \text{ atoms}}$

→ 1 formula unit of $KClO_3$ contains O atoms = 3
4.91×10^{23} formula units contain O atoms= $3 \times 4.91 \times 10^{23}$
= $\boxed{1.473 \times 10^{24} \text{ atoms}}$

Q11. Aspartame, the artificial sweetner has a molecular formulas of $C_{14}H_{18}N_2O_5$

(a) What is the mass of one mole of aspartame ($C_{14}H_{18}N_2O_5$)

Mass of one mole of aspartame = $(12 \times 14)+(1 \times 18)+(14 \times 2)+(16 \times 5)$
= $\boxed{294\ g}$

(b) How many moles are present in 52g of aspartame

Number of moles = $\frac{\text{Given Mass (in grams)}}{\text{Molar mass}}$

= $\frac{52}{294} = \boxed{0.177 \text{ moles}}$

(c) What is the mass in grams of 10.122 moles of aspartame

→ Number of moles of aspartame = 10.122 moles

→ $$\text{Number of moles} = \frac{\text{Given Mass (in grams)}}{\text{Molar mass}}$$

$$10.122 = \frac{\text{Mass}}{294}$$

$$\text{Mass} = 10.122 \times 294 = \boxed{2975.87\ g}$$

(d) How many hydrogen atoms are present in 2.43g of aspartame

→ Mass of aspartame = 2.43g

→ $$\text{Number of molecules} = \frac{\text{Given Mass (in grams)}}{\text{Molar mass}} \times N_A$$

$$= \frac{2.43}{294} \times 6.02 \times 10^{23}$$

$$= 4.97 \times 10^{21}\ \text{molecules}$$

→ 1 molecule of $C_{14}H_{18}N_2O_5$ contains H atoms = 18 atoms

4.97×10^{21} molecules contain H atoms $= 18 \times 4.97 \times 10^{21}$

$= \boxed{8.946 \times 10^{22}\ atoms}$

Q12. A sample of 0.600 mole of a metal M reacts completely with excess of fluorine to from 46.8g MF_2.

(a) How many moles of F are present in the sample of MF_2 that forms.

Solution:

→ Number of moles of M = 0.600 mol

Mass of MF_2 = 46.8 g

→ $$M + F_2 \longrightarrow MF_2$$

Compare the moles of M and MF_2 to find the moles of MF_2

M	:	MF_2
1 mole	:	1 mole
0.600 moles	:	0.600moles

Thus moles of MF_2 produced = 0.600 moles

→ 1 mole of MF_2 contains F moles = 2 moles

0.600 moles of MF_2 contain F moles $= 2 \times 0.600 = \boxed{1.2\ moles}$

(b) Which element is represented by the symbol M?

→ Mass of MF_2 produced = 46.86 g

Moles of MF_2 produced = 0.600 moles

→ 0.600 moles of MF_2 = 46.8 g

$$1\ \text{mole of}\ MF_2 = \frac{46.8}{0.600} = 78g$$

→ Formula mass of MF_2 = 78

Atomic mass of M + (19 × 2) = 78

Atomic mass of M = 78 − 38 = 40

Since *atomic mass of Ca is 40, therefore M is Ca.*

Q13. In each pair, choose the larger of the indicated quantity, or state if the samples are equal

(a) Individual particles: 0.4 moles of oxygen molecules or 0.4 atoms oxygen atoms.

(b) Mass: 0.4 mole of ozone molecules or 0.4 moles of oxygen atoms

(c) Mass: 0.6 mole of C_2H_4 or 0.6 moles of I_2

(d) Individual particles: 4.0g N_2O_4 or 3.3g SO_2

(e) Total ions: 2.3 moles of $NaClO_3$ or 2.0 moles of $MgCl_2$

(f) Molecules: 11.0g H_2O or 11.0 g H_2O_2

(g) Na^+ ion: 0.500 moles NaBr or 0.0145 kg NaCl

(h) Mass: 6.02×10^{23} atoms of ^{235}U or 6.02×10^{23} atoms ^{238}U

(a)

Both have same number of particles

Since both are equimolar quantities, therefore they have equal number of particles.

i.e. $0.4 \times 6.02 \times 10^{23} = 2.408 \times 10^{23}$ particles

(b)	(b)
For O_3 Moles of O_3 = 0.4 moles Molar mass of O_3 = 48 g mol^{-1} Mass = moles × molar mass = 0.4 × 48 = 19.2 g	For O Moles of O = 0.4 Atomic mass of O = 16 g mol^{-1} Mass = moles × atomic mass = 0.4 × 16 = 6.4 g

Hence, 0.4 moles of O_3 has greater mass than 0.4 moles of O

(c)	(c)
Number of moles = 0.6 Mass = moles × molar mass Molar mass of C_2H_4 = 28 g mol^{-1} Putting the values Mass of C_2H_4 = 0.6 × 28 = 16.8 g	Number of moles = 0.6 Mass = moles × molar mass Molar mass of I_2 = 2 × 126.9 = 253.8 g mol^{-1} Mass of I_2 = 0.6 × 253.8 = 152.28 g

Hence, 0.6 moles of I_2 has greater mass than 0.6 moles of C_2H_4

(d)	(d)
Mass of N_2O_4 = 4 g Molar mass of N_2O_4 = 28 + 64 = 92 g mol^{-1}	Mass of SO_2 = 3.3 g Molar mass of SO_2 = 32+32 = 64 g mol^{-1}

Number of molecules = $\frac{\text{Given Mass (in grams)}}{\text{molar mass}} \times N_A$

Number of molecules = $\frac{4}{92} \times 6.02 \times 10^{23}$

= 2.62×10^{22} molecules

Number of molecules = $\frac{\text{Given Mass (in grams)}}{\text{molar mass}} \times N_A$

Number of molecules = $\frac{3.5}{64} \times 6.02 \times 10^{23}$

= 3.1×10^{22} molecules

Hence, 5.5 g of SO_2 contains larger number of individual particles

(c)

Moles of Na_2CO_3 = 2.3

1 mole of Na_2CO_3 contains Na^+ ions = 6.02×10^{23}

2.3 moles will contain Na^+ = $2.3 \times 6.02 \times 10^{23}$ = 13.846×10^{23}

1 mole of Na_2CO_3 contains CO_3^{2-} ions = 6.02×10^{23}

2.3 moles will contain CO_3^{2-} = 13.846×10^{23}

Total ions = Na^+ ions + CO_3^{2-} ions

= [illegible] $\times 10^{23}$ + 13.846×10^{23}

= 2.7692×10^{24} ions

(d)

Moles of $MgCl_2$ = 2

1 mole of $MgCl_2$ contains Mg^{2+} ions = 6.02×10^{23}

2 moles will contain Mg^{2+} ions = $6.02 \times 10^{23} \times 2$ = 12.04×10^{23}

1 mole of $MgCl_2$ contains Cl^- ions = $2 \times 6.02 \times 10^{23}$

2 moles will contain Cl^- ions = $2 \times 2 \times 6.02 \times 10^{23}$ = 24.08×10^{23}

Total ions = Mg^{+2} ions + Cl^- ions = 12.04×10^{23} + 24.08×10^{23} = 3.612×10^{24} ions

Hence, 2 moles of $MgCl_2$ contain larger number of ions.

(f)

Mass of H_2O = 11.0 g

Molar mass of H_2O = 18 g mol^{-1}

Number of molecules = $\frac{\text{Given Mass (in grams)}}{\text{molar mass}} \times N_A$

Number of molecules of H_2O = $\frac{11}{18} \times 6.02 \times 10^{23}$

= 3.67×10^{23}

(f)

Mass of H_2O_2 = 11.0 g

Molar mass of H_2O_2 = 34 g mol^{-1}

Number of molecules = $\frac{\text{Given Mass (in grams)}}{\text{molar mass}} \times N_A$

Number of molecules of H_2O_2 = $\frac{11}{34} \times 6.02 \times 10^{23}$

= 1.926×10^{23}

Hence, 11.0 g of H_2O contains larger number of individual molecules

(g)

Moles of NaBr = 0.500

0.500 moles of NaBr contain 0.5 mole of Na^+ ions

Number of ions = moles × N_A

= $0.5 \times 6.02 \times 10^{23}$

= 3.01×10^{23} ions

(g)

Mass of NaCl = 0.0145 kg = 14.5 g

Molar mass of NaCl = 58.5 g mol^{-1}

Moles of NaCl = $\frac{\text{Given Mass (in grams)}}{\text{Molar mass}}$

= $\frac{14.5}{58.5}$ = 0.2478 moles

0.2478 moles of NaCl contain 0.2478 moles of Na^+ ions, therefore

Number of Na^+ ions = moles × N_A

= $0.2478 \times 6.02 \times 10^{23}$

= 1.49×10^{23}

Hence, 0.500 moles of NaBr contain larger number of Na^+ ions

(h)

6.02×10^{23} atoms means 1 mole, therefore

6.02×10^{23} atoms of ^{235}U = 235 g

(h)

6.02×10^{23} atoms means 1 mole, therefore

6.02×10^{23} atoms of ^{238}U = 238 g

Hence, 6.02×10^{23} atoms of ^{238}U have larger mass

Q14.

(a) Calculate the percentage of nitrogen in the four important nitrogen fertilizers i.e. NH_3, NH_2CONH_2, $(NH_4)_2SO_4$ and NH_4NO_3

Solution:

% is calculated by the formula

% of nitrogen = $\frac{\text{Mass of N atoms in the compound}}{\text{Molar mass of the compound}} \times 100$

(i) Molar Mass of NH_3 = $14 \times 1 + 1 \times 3 = 17$ g mol^{-1}

% of N in NH_3 = $\frac{14}{17} \times 100 = 82.35\%$

(ii) Molar Mass of NH_2CONH_2 = $14 \times 2 + 1 \times 4 + 12 \times 1 + 16 \times 1 = 60$ g mol^{-1}

% of N in NH_2CONH_2 = $\frac{28}{60} \times 100 = 46.67\%$

(iii) Molar Mass of $(NH_4)_2SO_4$ = $14 \times 2 + 1 \times 8 + 32 \times 1 + 16 \times 4 = 132$ g mol^{-1}

% of N in $(NH_4)_2SO_4$ = $\frac{28}{132} \times 100 = 21.21\%$

(iv) Molar Mass of NH_4NO_3 = $14 \times 2 + 1 \times 4 + 16 \times 3 = 80$ g mol^{-1}

% of N in NH_4NO_3 = $\frac{28}{80} \times 100 = 35\%$

(b) Calculate the percentage of nitrogen and phosphorous in each of the following.

(i) $NH_4H_2PO_4$ (ii) $(NH_4)_2HPO_4$ (iii) $(NH_4)_3PO_4$

Solution:

% of N and P are calculated by the formula

% of N or P = $\frac{\text{Mass of N or P atoms in the compound}}{\text{Molar mass of the compound}} \times 100$

(i) Molar mass of $NH_4H_2PO_4$ = $14 \times 1 + 1 \times 6 + 31 \times 1 + 16 \times 4 = 115$ g mol^{-1}

% of N in $NH_4H_2PO_4$ = $\frac{14}{115} \times 100 = 12.17\%$

% of P in $NH_4H_2PO_4$ = $\frac{31}{115} \times 100 = 26.96\%$

(ii) Molar mass of $(NH_4)_2HPO_4$ = $14 \times 2 + 1 \times 9 + 31 \times 1 + 16 \times 4 = 132$ g mol^{-1}

% of N in $(NH_4)_2HPO_4$ = $\frac{28}{132} \times 100 = 21.21\%$

% of P in $(NH_4)_2HPO_4$ = $\frac{31}{132} \times 100 = 23.35\%$

(iii) Molar mass of $(NH_4)_3PO_4 = 14 \times 3 + 1 \times 12 + 31 \times 1 + 16 \times 4 = 149\ g\ mol^{-1}$

$$\%\ \text{of N in}\ (NH_4)_3PO_4 = \frac{42}{149} \times 100 = 28.19\%$$

$$\%\ \text{of P in}\ (NH_4)_3PO_4 = \frac{31}{149} \times 100 = 20.80\%$$

Q15. Glucose $C_6H_{12}O_6$ is the most important in the cell for generating chemical potential energy. Calculate the mass % of each element in glucose and determine the number of C, H and O atoms in 10.5g of the sample.

Solution:

Molar mass of $C_6H_{12}O_6 = 12 \times 6 + 1 \times 12 + 16 \times 6 = 180\ g/mol$

$$\%\ \text{of an element} = \frac{\text{Mass of the element in compound}}{\text{Molarn mass of the compound}} \times 100$$

$$\%\ \text{of carbon} = \frac{72}{180} \times 100 = 40\%$$

$$\%\ \text{of hydrogen} = \frac{12}{180} \times 100 = 6.67\%$$

$$\%\ \text{of oxygen} = \frac{96}{180} \times 100 = 53.33\%$$

Mass of $C_6H_{12}O_6 = 10.5\ g$

$$\text{Molecules of}\ C_6H_{12}O_6 = \frac{\text{Given mass (in grams)}}{\text{Molar mass}} \times N_A$$

$$= \frac{10.5}{180g} \times 6.02 \times 10^{23}$$

$$= 3.5 \times 10^{22}\ \text{molecules}$$

1 molecule of $C_6H_{12}O_6$ contains C atoms $= 6$ atoms
3.5×10^{22} of $C_6H_{12}O_6$ contain C atoms $= 6 \times 3.5 \times 10^{22}$
$= \boxed{2.1 \times 10^{23}\ \textbf{atoms}}$

1 molecule of $C_6H_{12}O_6$ contain H atoms $= 12$ atoms
3.5×10^{22} of $C_6H_{12}O_6$ contain H atoms $= 12 \times 3.5\ 10^{22}$
$= \boxed{4.2 \times 10^{23}\ \textbf{atoms}}$

1 molecule of $C_6H_{12}O_6$ contain O atoms $= 6$ atoms
3.5×10^{22} of $C_6H_{12}O_6$ contain O atoms $= 6 \times 3.5 \times 10^{22}$
$= \boxed{2.1 \times 10^{23}\ \textbf{atoms}}$

Q16. Ethylene glycol is used in automobile antifreeze. It has 38.7% carbon, 9.7% hydrogen and 51.6% oxygen. Its molar mass is 62.1g mol^{-1}. Determine its empirical and molecular formula.

Solution:

ELEMENT	%	No. of gram atoms	Atomic Ratio	Empirical Formula
C	38.7	$\frac{38.7}{12} = 3.225$	$\frac{3.225}{3.225} = 1$	CH_3O
H	9.7	$\frac{9.7}{1.008} = 9.6$	$\frac{9.6}{3.225} = 3$	
O	51.6	$\frac{51.6}{16} = 3.225$	$\frac{3.225}{3.225} = 1$	

Thus Empirical Formula of Etylene Glycol is CH_3O

Empirical Formula mass $= (12 \times 1) + (3 \times 1) + (16 \times 1)$
$= 31\ g\ mol^{-1}$

Molecular mass $= 62.1\ g\ mol^{-1}$

$$n = \frac{\text{Molecular Mass}}{\text{Emprirical Mass}} = \frac{62.1}{31} = 2$$

Molecular Formula = n (Empirical Formula)
$= 2\ (CH_3O) = \mathbf{C_2H_6O_2}$

Q17. Serotenin ($M=176\ gmol^{-1}$) is a compound that conducts nerve impulses in brain and muscles. It contains 68.2% C, 6.86% H, 15.09% N, and 9.08% O. what is its molecular formula?

ELEMENT	%	No. of gram atoms	Atomic Ratio	Empirical Formula
C	68.20	$\frac{68.20}{12} = 5.7$	$\frac{5.7}{0.56} = 10$	$C_{10}H_{12}N_2O$
H	6.86	$\frac{6.86}{1.008} = 6.8$	$\frac{6.8}{0.56} = 12$	
N	15.09	$\frac{15.09}{14} = 1.07$	$\frac{1.07}{0.56} = 2$	
O	9.08	$\frac{9.08}{16} = 0.56$	$\frac{0.56}{0.56} = 1$	

Empirical Formula $= C_{10}H_{12}N_2O$

Empirical Formula mass $= (12\times10)+(1\times12)+(14\times2)+(16\times1) = 176\ g\ mol^{-1}$

Molecular mass $= 176\ g\ mol^{-1}$

$$n = \frac{\text{Molecular Mass}}{\text{Emprirical Mass}} = \frac{176}{176} = 1$$

Molecular Formula = n (Empirical Formula)
$= 1\ (C_{10}H_{12}N_2O) = C_{10}H_{12}N_2O$

Q18. An unknown metal M reacts with S to form a compound with a formula M_2S_3. If 3.12g of M reacts with exactly 2.88g of sulphur, what are the names of metal M and the compound M_2S_3?

Solution:

→ The reaction can be written as $2M + 3S \rightarrow M_2S_3$

→ Mass of S in $M_2S_3 = 32\times 3 = 96\ g$
According to the given data
2.88g of S react with M = 3.12 g
96g of S react with M $= \frac{3.12g}{2.88g}\times 96g = 104g$

→ Thus according to formula M_2S_3
2 moles of M = 104 g of M
1 mole of M $= \frac{104}{2} = 52\ g\ mol^{-1}$

Hence Atomic mass of M $= 52\ g\ mol^{-1}$
Since $52\ g\ mol^{-1}$ is the atomic mass of chromium,
Therefore M is chromium and M_2S_3 is Cr_2S_3 i.e., chromium sulphide.

Q19. The octane present in gasoline burns according to the following equation.

$$2C_8H_{18} + 25O_2 \rightarrow 16CO_2 + 18H_2O$$

(a) How many moles of O_2 are needed to react fully with 4 moles of octane?

Solution:

The balanced chemical equation for the chemical reaction is

$$2C_8H_{18} + 25O_2 \longrightarrow 16CO_2 + 18H_2O$$

Moles of octane = 4 moles

Compare C_8H_{18} and O_2 according to balanced chemical equation.

C_8H_{18} : O_2

2 moles : 25 moles

Therefore 4 moles : $\frac{25}{2}\times 4 = 50$moles

Hence Moles of O_2 required = $\boxed{\textbf{50 moles}}$

(b) How many moles of CO_2 can form one mole of octane?

Moles of octane = 1 mole

Compare C_8H_{18} and CO_2 according to balanced chemical equation.

C_8H_{18} : CO_2

2 moles : 16 moles

Therefore 1 mole : $\frac{16}{2}\times 1 = 8$moles

Hence Moles of CO_2 can be produced = $\boxed{\textbf{8 moles}}$

(c) How many moles of water produced by the combustion of 6 moles of octane?

Moles of octane = 6 moles

Compare C_8H_{18} and H_2O according to balanced chemical equation.

C_8H_{18} : H_2O

2 moles : 18 moles

Therefore 6 moles : $\frac{18}{2}\times 6 = 54$ moles

Hence Moles of H_2O produced = 54 moles

(d) If this reaction is to be used to synthesize 8 moles of CO_2, how many grams of oxygen are needed? How many grams of octane will be used?

Moles of CO_2 = 8 moles

Compare CO_2 and O_2 according to balanced chemical equation.

CO_2 : O_2

16 moles : 25 moles

8 moles : $\frac{25}{16}\times 8 = 12.5$moles

Hence Moles of O_2 required = 12.5 moles
And Mass of O_2 required $= 12.5\times 32 = \boxed{400g}$

Compare CO_2 and C_8H_{18} according to balanced chemical equation.

CO_2	:	C_8H_{18}
16 moles	:	2 moles
Therefore 8 moles	:	$\frac{2}{16} \times 8 = 1$ mole

Hence Moles of octane used = 1 mole

And Mass of octane used = 1 × 114 = $\boxed{114\ g}$

Q20. Calculate the number of gram of Al_2S_3, which can be prepared by the reaction of 20.00g of Al and 30.00g of sulphur. How much non-limiting reactant is in excess? *(Lahore Board, 2013)*

Solution:

→ The balanced chemical equation for the chemical reaction is

$$2Al + 3S \longrightarrow Al_2S_3$$

Given mass of Al = 20 g

Number of moles of Al = $\frac{20}{27} = 0.74$ moles

Given mass of S = 30 g

Number of moles of S = $\frac{30}{32} = 0.9375$ moles

→ *Determination of Limiting Reactant*

Compare Al and Al_2S_3 according to balanced chemical equation.

Al	:	Al_2S_3
2 moles	:	1 mole
Therefore 0.74 moles	:	$\frac{1}{2} \times 0.74 = 0.37$ moles

Hence number of moles of the product produced by Al = 0.37 moles

Compare S and Al_2S_3 according to balanced chemical equation.

S	:	Al_2S_3
3 moles	:	1 moles
0.9375 moles	:	$\frac{1}{3} \times 0.9375 = 0.3125$ moles

Hence number of moles of the Al_2S_3 produced by S = 0.3125 moles

→ Since S produces least number of moles of the product, therefore it is the limiting reactant.

Hence Moles of Al_2S_3 produced = 0.3125 moles

Mass of Al_2S_3 produced = 0.3125 × 150 = $\boxed{46.87\ g}$

→ *Determination of amount of Al left unreacted*

$$2Al + 3S \longrightarrow Al_2S_3$$

Compare the moles of S and Al to find the moles of Al reacted.

S	:	Al
3 moles	:	2 moles
0.9375 moles	:	$\frac{2}{3} \times 0.9375 = 0.625$ moles

→ Moles of Al consumed = 0.625 moles

Moles of Al taken = 0.74 moles

Moles of Al left unreacted = 0.74 − 0.625 = 0.115 moles

Mass of Al left unreacted = 0.115 × 27 = $\boxed{3.105g}$

Q21. A mixture of two liquids, hydrazine N_2H_4 and N_2O_4 are used as fuel in rockets. They produce N_2 and water vapours. How many grams of N_2 gas will be formed by reacting 100g of N_2H_4 and 200g of N_2O_4.

Solution:

→ The balanced chemical equation for the chemical reaction is

$$2N_2H_4 + N_2O_4 \longrightarrow 3N_2 + 4H_2O$$

Given mass of N_2H_4 = 100 g

Number of moles of N_2H_4 = $\frac{100}{32} = 3.125$ moles

Given Mass of N_2O_4 = 200 g

Number of moles of N_2O_4 = $\frac{200}{92} = 2.17$ moles

→ *Determination of Limiting Reactant*

Compare N_2H_4 and N_2 according to balanced chemical equation.

N_2H_4	:	N_2
2 moles	:	3 moles
3.125 moles	:	$\frac{3}{2} \times 3.125 = 4.69$ moles

Compare N_2O_4 and N_2 according to balanced chemical equation.

N_2O_4	:	N_2
1 mole	:	3 moles
Therefore 2.17 moles	:	$\frac{3}{1} \times 2.17 = 6.51$ moles

→ Since N_2H_4 produce least number of moles of the product, therefore it is the limiting reactant.

Hence Moles of the product produced = 4.69 moles

And Mass of the product produced $= 4.69 \times 28 = \boxed{131.32\ g}$

Q22. Silicon carbide (SiC) is an important ceramic material. It is produced by allowing sand (SiO_2) to react with carbon at high temperature.

$$SiO_2 + 3C \rightarrow SiC + 2CO$$

When 100kg sand is reacted with excess of carbon, 51.4kg of SiC is produced. What is the percentage yield of SiC?

Solution:

→ The balanced chemical equation for the chemical reaction is

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Mass of SiO_2 = 100 kg = 100000g

Number of moles of $SiO_2 = \dfrac{100000}{60} = 1666.67$ moles

→ Compare SiO_2 and SiC according to balanced chemical equation.

SiO_2	:	SiC
1 mole	:	1 mole
Therefore 1666.67 moles	:	1666.67 moles

Thus

Moles of SiC, expected to be produced= 1666.67 moles

Molar mass of SiC=28+12=40 g/mol

Mass of SiC, expected to be produced$= 1666.67 \times 40 = 66666.8$ g

→ Thus Theoretical yield of SiC= 66666.8 g

Actual yield of SiC = 51.4 kg = 51400 g

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

$$= \frac{51400}{66666.8} \times 100 = \boxed{77\%}$$

HELLO! Mr. Question here!

Multiple Choice Questions from PAST PAPERS

1. An ordinary microscope can measure the size of object upto: *(Faisalabad Board, 2007)*
   (a) 100 nm (b) 200 nm (c) 400 nm (d) 500 nm
2. How many times a haemoglobin molecule is heavier than hydrogen atom *(Faisalabad Board, 2010)*
   (a) 38000 times (b) 58000 times (c) 68000 times (d) 88000 times
3. Which of the following element can exist in monoatomic form? *(Multan Board, 2011)*
   (a) oxygen (b) chlorine (c) nitrogen (d) helium
4. Atom of which of the following element has independent existence *(Bahawalpur Board, 2011)*
   (a) Fluorine (b) Krypton (c) Oxygen (d) Nitrogen
5. A Swedish chemist J. Berzelius determined *(Sargodha Board, 2013)*
   (a) atomic number (b) atomic mass (c) molecular mass (d) ionic mass
6. Electrometer is also called *(Lahore Board, 2007)*
   (a) Voltmeter (b) Avometer (c) Ion Collector (d) Galvanometer
7. Height of peak in mass spectrum shows: *(Lahore Board, 2008; Multan Board, 2013)*
   (a) Number of isotopes (b) Mass number
   (c) Relative abundance (d) Number of protons
8. Silver has isotopes: *(Lahore Board, 2010)*
   (a) 9 (b) 16 (c) 17 (d) 18
9. One a.m.u. is equal to *(Lahore Board, 2011)*
   (a) 1.661×10^{27} kg (b) 1.661×10^{-27} kg (c) 1.661×10^{-24} kg (d) 1.661×10^{24} kg
10. Out of 280 isotopes which occur in nature, the radioactive isotopes are *(Rawalpindi Board, 2008)*
    (a) 116 (b) 126 (c) 30 (d) 40
11. The number of isotopes of tin are *(Lahore Board, 2011; Rawalpindi Board, 2011, 2013)*
    (a) 6 (b) 9 (c) 11 (d) 14
12. The number of molecules in one gram atom of CO_2 is: *(Gujranwala Board, 2010)*
    (a) 6.02×10^{23} (b) 6.02×10^{22} (c) 6.27×10^{27} (d) 6.02×10^{24}
13. Empirical formula of glucose is: *(Gujranwala board, 2011)*
    (a) CHO (b) $C_2H_4O_2$ (c) CH_2O (d) $C_6H_{12}O_6$
14. The mass of CO_2 containing 8 grams of oxygen (O_2) in grams is: *(Gujranwala board, 2011)*
    (a) 32 (b) 22 (c) 16 (d) 11

15. Who determined the atomic mass? (Multan Board, 2011)
(a) Maxwell (b) John Dalton (c) Newton (d) J-Berzelius

16. The percentage of Nitrogen in Ammonia is: (Multan Board, 2013)
(a) 82.35% (b) 46.67% (c) 92% (d) 78%

17. Molecular mass of $CaCO_3$ is: (Lahore Board, 2009)
(a) 100 (b) 90 (c) 120 (d) 106

18. Percentage of oxygen in water is (Lahore Board, 2009)
(a) 80% (b) 88.89% (c) 8.8% (d) 9.8%

19. The number of isotopes of oxygen is: (Bahawalpur Board, 2009)
(a) One (b) Two (c) Four (d) Three

20. Isotopes are sister atoms of same element with similar chemical properties but different (Rawalpindi Board, 2009)
(a) Atomic number (b) Atomic volume (c) Atomic weight (d) Atomic structure

21. The volume occupied by 4.4g of CO_2 at STP is (Sargodha Board, 2010)
(a) 2.24 dm^3 (b) 22.4 dm^3 (c) 112 cm^3 (d) 1.12 dm^3

22. The pressure of vapours maintained in ionization chamber of mass spectrometer during isotopic analysis is (Sargodha Board, 2010)
(a) 10^{-2} torr (b) around 10^{-6} torr (c) around 10^{-7} torr (d) 10^{-9} torr

23. The number of isotopes of Cd is: (Bahawalpur Board, 2010)
(a) 6 (b) 2 (c) 9 (d) 11

24. The mass of an oxygen atom is (Rawalpindi Board, 2010)
(a) 2.657×10^{-23} g (b) 2.675×10^{23} g (c) 16 g (d) 32g

25. One of the substance is used to absorb CO_2 gas in combustion analysis which is that substance. (D.G. Khan Board, 2010)
(a) 50% KOH (b) Al_2O_3 (c) $Mg(ClO_4)_2$ (d) SiO_2

26. Percentage of N in NH_3 is (Faisalabad Board, 2011)
(a) $\frac{14}{17} \times 100$ (b) $\frac{14}{34} \times 100$ (c) $\frac{3}{17} \times 100$ (d) $\frac{3}{34} \times 100$

27. In combustion analysis, H_2O vapours are absorbed by: (Lahore Board, 2007)
(a) 50% KOH (b) $Mg(ClO_4)_2$ (c) NaOH (d) $MgCl_2$

28. Positive ions are called: (Lahore Board, 2009)
(a) Cations (b) Anions (c) Molecules (d) Hydrated ions

29. The volume occupied by 28 g of N_2 at STP is (Rawalpindi Board, 2010)
(a) 22.414 dm^3 (b) 2.2414 dm^3 (c) 224.14 dm^3 (d) 1.12 dm^3

30. How many isotopes are present in palladium? (Sargodha Board, 2014)
(a) Four (b) Five (c) Six (d) Seven

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(d)	2	(c)	3	(d)	4	(b)	5	(b)
6	(c)	7	(c)	8	(a)	9	(b)	10	(d)
11	(c)	12	(a)	13	(c)	14	(d)	15	(d)
16	(a)	17	(a)	18	(b)	19	(d)	20	(c)
21	(a)	22	(c)	23	(c)	24	(a)	25	(a)
26	(a)	27	(b)	28	(a)	29	(a)	30	(c)

Detailed Explanation of Past Papers MCQs & answers to all Past Papers SHORT QUESTONS in
COLLEGE CHEMISTRY OBJECTIVE BOOK-I

SHORT & LONG QUESTIONS FROM PAST PAPERS

ATOM, HISTORY OF ATOM, EVIDENCE FOR AN ATOM, MOLECULE

Short Questions

(1) *Write down the main postulates of Dalton's Atomic Theory* (Faisalabad Board, 2008)
(2) *Why atoms cannot be observed by an ordinary optical microscope?* (Rawalpindi Board, 2013)
(3) *Differentiate between homo-atomic and hetero-atomic molecule with example.* (D.G. Khan Board, 2011)
(4) *Define the term molecule. Give two examples.* (Gujranwala Board, 2013)

Long Questions

(1) *Define with example, atomicity, molecular formula, Avogadro's number.* (Multan Board, 2012)

ION, MOLECULAR ION

Short Questions

(1) *Describe briefly the energy changes taking place during formation of positive and negative ions.* (D.G. Khan Board, 2009) OR *Explain formation of ions with respect to energy changes* (Multan Board, 2008)
(2) *Formation of uni-negative ion is an exothermic process. Justify.* (Multan Board, 2007)
(3) *Define ion and give two examples* (Sargodha Board, 2011)
(4) *What is molecular ion? Give an example* OR *What do you mean by molecular ion?* (Bahawalpur Board, 2012: Lahore Board, 2012: Sargodha Board, 2009, 2010, 2012)
(5) *Define molecular ion, write its uses* (Lahore Board, 2014)
(6) *Define molecular ion. How is it generated?* (Multan Board, 2012: Sargodha Board, 2013)

RELATIVE ATOMIC MASS

Short Questions

(1) Define Relative atomic mass and give its S.I. units. **(Bahawalpur Board, 2010)**
(2) What is the atomic mass uit? Give its value in grams. **(Faisalabad Board, 2009: Gujranwala Board, 2011: Sargodha Board, 2009)**

ISOTOPES

Short Questions

(1) What are isotopes? How relative atomic masses of Isotopes are determined? **(Multan Board, 2008, 2011)**
(2) Why the isotopes have same chemical properties? **(Multan Board, 2009: Rawalpindi Board, 2007, 2009)**
(3) What are monoisotopic elements? Give two examples **(Rawalpindi Board, 2013)**
(4) What is the relative abundance of isotopes? How is it determined? **(D.G. Khan Board, 2010)**

Long Questions

(1) What are isotopes? How do you deduce the fractional atomic masses of elements from the relative isotopic abundance? Give one example. **(Faisalabad Board, 2008: Lahore Board, 2009)**
(2) Explain relative abundance of isotopes with suitable examples. **(Faisalabad Board, 2011)**

MASS SPECTROMETRY

Short Questions

(1) What is the function of electrometer in separation of isotopes in mass spectrometer? **(Faisalabad Board, 2009: Gujranwala Board, 2008)**
(2) Explain mathematical relationship for m/e of an ion in mass spectrometry **(Lahore Board, 2011)**
(3) What is mass spectrum? **(Lahore Board, 2013)**
(4) No individual Ne atom in the sample of elements has mass of 20.18 amu. Explain Why **(Bahawalpur Board, 2012: Faisalabad Board, 2012: Lahore Board, 2014)** OR Atomic mass may be written in fractions, Why? **(Bahawalpur Board, 2009: Multan Board, 2008, 2010: D.G. Khan Board, 2009: Lahore Board, 2008: Sargodha Board, 2009)**

Long Questions

(1) What is mass spectrometer? How is it used to determine the relative atomic masses of isotopes. **(Gujranwala Board, 2012, 2014: Rawalpindi Board, 2009: Lahore Board, 2008: Sargodha Board, 2009: D.G. Khan Board, 2012)**
(2) Discuss the mass spectrometer to do the analysis of isotopes of an element. Mention the roles of electric and magnetic fields to separate the isotopes of an element **(Multan Board, 2007)**
(3) How the isotopes of an elements are separated by mass spectrometer **(Multan Board, 2013)**

EMPIRICAL FORMULA, MOLECULAR FORMULA, COMBUSTION ANALYSIS

Short Questions

(1) Give the main points for the determination of molecular formula. **(Multan Board, 2013)**

(2) Define Molecular and Empirical Formula with examples **(Bahawalpur Board, 2009: Multan Board, 2009: Lahore Board, 2007, 2013)**
(3) Molecular formula is multiple of empirical formula. Explain with example. **(D.G. Khan Board, 2010: Multan Board, 2009, 2011)**
(4) Differentiate between empirical and molecular formula **(Faisalabad Board, 2012: Lahore Board, 2012: Sargodha Board, 2012 [as part of long question])**
(5) **COMBUSTION ANALYSIS**
(6) Write formulas used for the determination of percentage of C & H. **(Faisalabad Board, 2013), (Sargodha Board, 2012)**
(7) Write functions of $Mg(ClO_4)_2$ and KOH in combustion analysis **(Lahore Board, 2014)**

Long Questions

(1) Write down the steps required to find the empirical formula of a compound. **(Gujranwala Board, 2008: Bahawalpur Board, 2009: Lahore Board, 2014: Multan Board, 2008: Gujranwala Board, 2010)**
(2) What is combustion analysis? How the percentages of various elements present in an organic compound are determined? **(D.G. Khan Board, 2008: Bahawalpur Board, 2012: D.G. Khan Board, 2009: Gujranwala Board, 2006)** OR Give a method for the determination of the % of carbon and hydrogen in the given organic compound **(Lahore Board, 2006)**
(3) What is empirical formula? Discuss how empirical formula is determined by combustion analysis. **(Faisalabad Board, 2009: Sargodha Board, 2014) (Gujranwala Board, 2005: Multan Board, 2010: Rawalpindi Board, 2009)**

MOLE, AVOGADRO'S NUMBER, MOLAR VOLUME

Short Questions

(1) Define gram molecule and gram formula. **(Gujranwala Board, 2009)**
(2) NaCl has 58.5 amu as formula mass and not the molecular mass. Justify? **(Multan Board, 2009: Sargodha Board, 2009: Rawalpindi Board, 2007)**
(3) Define Avogadro's Number. Give its numerical value? **(Bahawalpur Board, 2012: D.G. Khan Board, 2008: Multan Board, 2007)**
(4) Define Avogadro's number. How does it relate to the masses of chemical substances?
(5) Define molar volume. Give two examples. **(D.G. Khan Board, 2009)**
(6) One mole of different gases has different masses but occupies same volume. Why? **(D.G. Khan Board, 2010)**
(7) Define (a) molar volume (b) molecular formula **(Rawalpindi Board, 2012)**

Long Questions

(1) Define the followings giving one example of each **(Multan Board, 2008, 2009)**
(2) (a) gram atom (b) gram ion
(3) Define and explain the concept of Mole and Avogadro's number with examples. **(Faisalabad Board, 2012)**
(4) Write a note on Avogadro's number. **(Multan Board, 2012)**

STOICHIOMETRY

Short Questions

(1) Give two stoichiometric assumptions. (Bahawalpur Board, 2010), (Lahore Board, 2009), (Gujranwala Board, 2011) (Rawalpindi Board, 2013; Lahore Board, 2014)

(2) State law of conservation of mass. (Bahawalpur Board, 2010)

(3) Law of conservation of mass has to be obeyed during stoichiometric calculations. Give reason or Comment on it. (D.G. Khan Board, 2008; Lahore Board, 2013)

(4) What is stoichiometery and define yield of a chemical reaction? (Faisalabad Board, 2007)

(5) Give the assumptions of stoichiometric calculations. (Faisalabad Board, 2008)

(6) Define stoichiometry and write down its basic assumptions (Faisalabad Board, 2010), (Rawalpindi Board, 2008), (Sargodha Board, 2013)

(7) Which laws are to be considered during stoichiometric calculations? (Gujranwala Board, 2009)

(8) Write two assumption of stoichiometry (Gujranwala Board, 2011, 2014; Lahore Board, 2014; Multan Board, 2007)

(9) By using a balanced chemical equation, what type of relationships can be studied? (Multan Board, 2011)

Long Questions

(1) State conditions of stoichiometry (Rawalpindi Board, 2011)

(2) What is stoichiometry? Give assumption. Mention two improtat lwas, which help to perform the stoichiometric calculations. (04) (Lahore Board, 2014; Rawalpindi Board, 2012)

LIMITING REACTANT

Short Questions

(1) How limiting reactant controls the amount of products formed? (Faisalabad Board, 2007)

(2) List steps involved to identify a limiting reactant (Faisalabad Board, 2011; Multan Board, 2010)

(3) How the limiting reactant is identified? (Gujranwala Board, 2009), (Sargodha Board, 2013)

(4) Define limiting reactant, give an example. (Lahore Board, 2011)

(5) What is limiting reactant? Write the steps for identification of a limiting reactant. (Multan Board, 2009), (Rawalpindi Board, 2010)

(6) Define limiting reactant. How LR is identified? (Sargodha Board, 2012)

Long Questions

(1) Define limiting reactant. How it controls the amount of products? Give example (Sargodha Board, 2009)

(2) What is limiting reactant. Write the steps to identify a limiting reactant. How it controls the amount of products with example. (D.G. Khan Board 2012; Azad Kashmir Board, 2012)

YIELD

Short Questions

(1) Actual yield is usually less than theoretical yield. Why? (Bahawalpur Board, 2011), (Rawalpindi Board, 2012) (Gujranwala Board, 2007), (Gujranwala Board, 2008, 2012), (Multan Board, 2013), (Rawalpindi Board, 2010)

(2) Why the experimental yield is always less than theoretical yield? (Faisalabad Board, 2012), (Lahore Board, 2008), (Multan Board, 2007), (Multan Board, 2010) OR What are the reasons for low actual yield than the theoretical yield of reactions? (Multan Board, 2008) OR Why theoretical yield is greater than actual yield? (Lahore Board, 2013), (Multan Board, 2009)

(3) How can the efficiency of a chemical reaction be expressed? (Gujranwala Board, 2005; Lahore Board, 2007)

(4) Why we calculate %age yield? (Lahore Board, 2014)

(5) Distinguish between theoretical and experimental yield. (Rawalpindi Board, 2009)

Long Questions

(1) Define actual yield. Write formula for the calculation of percentage yield. (Lahore Board, 2010)

(2) What is the difference between actual yield ad theoretical yield? Why actual yield is less than theoretical yield?(04) (Lahore Board, 2012)

(3) What do you mean by the terms: (i) Isotope (ii) Empirical formula (iii) Gram atom (iv) Yield of a chemical reaction. (Multan Board, 2009)

(4) Define isotopes (Lahore Board, 2012, Multan Board, 2009→(as a part of long question))

(5) Define yield. How do we calculate the percentage yield of a chemical reaction? (Gujranwala Board, 2009)

TEST YOUR SKILLS

Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) 14.20 litres of H_2 gas at STP weighs
(a) 12.2 g (b) 448 g $\boxed{\text{(c) 1.28 g}}$ (d) 20 g

(ii) How many g of H_2SO_4 are present in 0.25 mole of H_2SO_4
(a) 2.45 $\boxed{\text{(b) 24.5}}$ (c) 0.245 (d) 0.25

(iii) 1 amu is equal to
(a) 1.661×10^{-27} g $\boxed{\text{(b) } 1.661 \times 10^{-24} \text{ g}}$ (c) 1.6×10^{-23} (d) none

(iv) Height of peak in mass spectrum show
(a) Number of isotopes (b) Mass number $\boxed{\text{(c) relative abundance}}$ (d) Number of protons

(v) The average atomic mass of Neon is
(a) 20 amu (b) 22.18 amu (c) 21.18 amu $\boxed{\text{(d) 20.18 amu}}$

(vi) The moles of Mg present in a sample containing 1×10^{22} Mg atoms will be
(a) $\boxed{0.017}$ (b) 0.17 (c) 1.7 (d) 17

(vii) How many grams of magnesium contain the same no. of atoms as 0.5 g of carbon?
(a) 0.5 g $\boxed{\text{(b) 1 g}}$ (c) 0.25 g (d) none

(viii) How many moles of oxygen atoms are present in 0.4 moles of oxygen gas?
(a) 2.4×10^{23} (b) 4.916 $\boxed{\text{(c) 0.8}}$ (d) 4.5

(ix) The no. of molecules in 64 g of sulphur is
$\boxed{\text{(a) } 2N_A}$ (b) $16N_A$ (c) $0.25N_A$ (d) none

(x) The modern atomic mass scale is based on
(a) H – 1 $\boxed{\text{(b) C – 12}}$ (c) C – 14 (d) O – 16

(xi) The number of isotopes of Cadmium is
(a) 3 $\boxed{\text{(b) 9}}$ (c) 6 (d) 11

(xii) Which of the following molecular ions are more abundent?
$\boxed{\text{(a) cationic ions}}$ (b) Anionic ions (c) Halide ions (d) alkali metal ions

(xiii) One mole of CH_3COOH contains the number of H-atoms
(a) 6.02×10^{23} $\boxed{\text{(b) } 2.41 \times 10^{24}}$ (c) 1.81×10^{24} (d) 6.02×10^{24}

(xiv) A limiting reactant gives
$\boxed{\text{(a) minimum number of moles of the product}}$ (b) maximum number of moles of the produc
(c) zero moles of the product (d) none

(xv) The quantitative relationships between the reactants and products, according to balanced chemical equation is called
(a) percentage yield $\boxed{\text{(b) stoichiometry}}$ (c) limiting reacting (d) percentage composition

(xvi) A molecule of haemoglobin is 68,000 times heavier than one atom of
(a) F $\boxed{\text{(b) H}}$ (c) P (d) O

(xvii) Which of the following species are produced in the ionization chamber of mass spectrometer?
(a) F^-, O^{2-}, Ne^- (b) F_2, O_2, Ne $\boxed{\text{(c)}}$ F_2^+, O_2^+, Ne^+ (d) F^+, O^+, Ne^+

SUBJECTIVE

Time: 2:10 Hours **Marks. 68**

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question number carefully. **(22 x 2)=44**

Section - I

Q2. Answer any Eight parts from the followings.

(i) Prove that one atom of Mg is twice as heavy as an atom of carbon.
(ii) Law of conservation of mass has to be obeyed during stiochiometric calculations. Explain
(iii) One mole of different compounds has different masses but has the same number of molecules. Why?

(iv) Differentiate between empirical and molecular formula.
(v) What is the basic principle of mass spectrometry?
(vi) What do you mean by molecular ion?
(vii) What is atomic mass unit?
(viii) Molecular formula is a multiple of empirical formula. Justify it.
(ix) 22.414 dm^3 of each gas at STP has a different mass but the same number of molecules. Why?
(x) Calculate the mass of 10^{-3} moles of $MgSO_4$
(xi) Formation of a positive ion is an endothermic process. Why?
(xii) N_2 and CO have the same numbers of electrons protons and neutrons explain with reason.?

Q3. Answer any Eight parts from the followings.

(i) Why electron microscope is used to see the atoms?
(ii) The atomic masses may be in fraction why?
(iii) Why limiting reactants control the amount of product during the chemical reaction?
(iv) What is the function of KOH in combustion analysis?
(v) Why relative atomic masses of the elements are in fractions?
(vi) What is the pressure of vapours in the ionization chamber of mass spectrometer?
(vii) How positive ions are separated in mass spectrometer?
(viii) How positive ions are accelerated in mass spectrometer?
(ix) What is the position of isotopes of an element in the periodic table?
(x) What is an electrometer?
(xi) Which five elements make 50% of the earth crust ?
(xii) One mole of each N_2, CO_2 and H_2 contain equal number of molecules. Give reason?

Q4. Answer any Six parts from the followings.

(i) In combustion analysis how the percentage of CO_2 is measured?
(ii) A compound has empirical formula HO and its molecular mass is 34. What is its molecular formula?
(iii) The relative abundance of isotopes of B is $^{10}_{5}B$ = 20.002% and $^{11}_{5}B$ = 79.992%. What is its relative atomic mass?
(iv) Calculate the mole of Chlorine atoms in 0.882 g C_6H_4Cl?
(v) How many moles are their in equal masses of C and Mg?
(vi) NaCl has 58.5 a.m.u as formula mass and not the molecular mass. Justify it?
(vii) Calculate the mass in grams of 2.74 moles of $KMnO_4$?
(viii) How percentage yield is calculated?
(ix) Theoretical yield is less than actual yield. why?

Section - II (Attempt any three questions) (8 x 3)=24

Q5. (a) What is limiting reactant? How can you determine it. Explain it with a chemical reaction. (03)
(b) What is an atom? What is its evidence? (03)
(c) Calculate the percentage of N and P in $(NH_4)_3PO_4$ (02)

Q6. (a) What is stoichiometry? What are its assumptions? (03)
(b) Define the following with examples (i) Gram atom (ii) Gram formula (03)
(c) Most of the elements have fractional atomic masses. Why? (02)

Q7. (a) Describe combustion analysis for determination of percentages of C, H and O in an organic compound. (04)
(b) NH_3 gas can be prepared by heating together two solids. NH_4Cl and $Ca(OH)_2$ if a mixture containing 100g of each solid is heated them calculate the number of grams of NH_3 produced. (04)
$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2NH_3 + 2H_2O$ (Atomic mass of Ca = 40 and Cl = 35)

Q8. (a) Calculate the number of grams of K_2SO_4 and water produced when 14g of KOH are reacted with excess of H_2SO_4 also calculate the number of molecules of water produced? (3½)
(b) Define with examples (i) Relative atomic mass (ii) Isotopes (iii) Ion (4½)

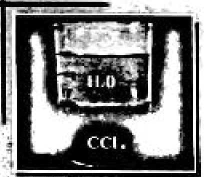
Q9. (a) What is mass spectrum? Describe briefly. (02)
(b) Serotonin (M = 176 $g\,mol^{-1}$) is a compound that conducts nerve impulses in brain and muscles. It contains 68.2% C, 6.86% H, 15.09% N, and 9.08% O. what is its molecular formula? (03)
(c) If 9.8 g of H_2SO_4 are dissolved in water, how many negative ions, positive ions, negative charges and positive charges will be there in the solution? (03)

Things to Remember

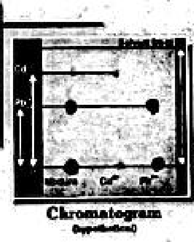
Chapter 2

EXPERIMENTAL TECHNIQUES IN CHEMISTRY

Separating Funnel



Distribution of I_2 between H_2O and CCl_4



Chromatogram

Sintered Glass Crucible

CONTENTS

INTORDUCTION

Analytical Chemistry

The branch of chemistry, which deals with the study of analytical methods for qualitative and quantitative analysis of chemical substances.

Qualitative Analysis

It deals with the identification of elements, present in a substance.

Quantitative Analysis

It deals with the determination of relative amounts of the elements present in a substance.

A complete quantitative analysis involves the following steps

1. Obtaining a sample
2. Separation of the desired constituent
3. Measurement and calculation of results
4. Drawing conclusion.

Methods for Separating the Desired Constituent

Following techniques are commonly used for separating the desired constituent.

A. Filtration B. Crystallization
C. Sublimation D. Solvent Extraction
E. Chromatography.

FILTRATION

The process of separation of insoluble solid particles from liquids by passing them through a filter medium is called filtration.

- The insoluble solid particles obtained after filtration is called Residue.
- During filtration, the liquid that passes through the filter medium is called Filtrate.
- The medium used for filtration is called filter medium.

Types of Filter Media

The choice of filter media depends upon the nature of precipitate and some other factors.

Two types of filter media are generally used

(1) Filter paper (2) Filter crucibles

(1) Filter Paper

A paper used for filtration is called filter paper.

Filter papers of different porosities (pore size) are available. The choice of a filter paper depends upon the size of particles in precipitates.

Whatmann filter paper No. 41 & 42 are in common use.

Method of Filtration by Glass Funnel and Filter Paper

Figure Filtration assembly

- Filtration by a glass funnel and filter paper is usually slow.
- The liquid containing solid particles is poured on a glass rod which then goes into the filter paper.
- The residue is collected on filter paper and filtrate collected in the beaker as shown in fig.

Points For a Good Filtration Process

Property of Filter Paper:

(a) The filter paper must be so large that it is ¼ to ½ full of the total precipitate at the end of filtration.

Properties of Funnel:

(b) The funnel should be so large that its upper rim is approximately 2 cm above the edge of filter paper.

(c) The stem of the funnel should be several cm long, so that, it goes down into the beaker.

Precaution

(d) To run filtration smoothly, the stem of funnel is kept full of liquid, till there is liquid present in conical part of the funnel

(e) The tip of the stem of funnel should touch the side of beaker, so that the filtrate runs down the side of beaker without splashing.

Folding of Filter Paper

Following are important points.

The filter paper should be folded twice

(a) First fold the paper in half along the diameter of the paper.

(b) Second fold the paper in half again, such that edges of the paper do not quite match

(c) Open the paper on a slightly larger section such that three fold thickness is on one half side and one fold thickness is on other half side and apex angle, slightly greater than 60°.

(d) Wet the filter paper with water, insert into a 60° degree funnel and firmly press down.

Methods to increase the Rate of Filtration

(i) Suction Filtration

The ordinary filtration is very slow. To increase the rate of filtration suction is applied. This is called suction filtration or vacuum filtration. For better suction filtration, filter paper must be tightly pressed.

(ii) Fluted Filter Paper

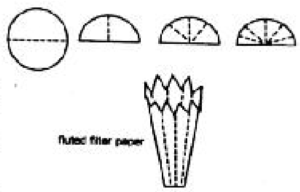


Figure Fluted filter paper

- By using fluted filter paper rate of filtration through a conical funnel can be increased.
- To prepare it, ordinary filter paper is folded in such a way that a fan like arrangement is obtained.
- This fan like arrangement has alternate ups and downs.
- Thus, surface area is increased and hence rate of filtration is increased.

(2) Filter Crucibles

For suction filtration, filter crucibles are commonly used.

Two types of filter crucibles are generally used.

(a) Gooch Crucible

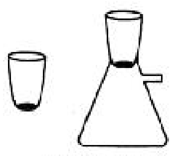


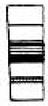
Figure Gooch crucible with filtering apparatus

- It is made up of porcelain having a perforated bottom.
- The perforated bottom is covered with filter paper or with paper pulp.
- For quick filtration, Gooch crucible is fitted into a suction filtration apparatus.
- It is useful for filtration of precipitates, which need to be ignited at high temperature.
- Some materials, e.g. conc. HCl, $KMnO_4$ solution react with filter paper. Therefore, they cannot be filtered using filter paper. For such materials, Asbestos Mat is used in place of filter paper.

(b) Sintered Glass Crucible

It is a glass crucible. It has a porous sintered glass disc sealed into its bottom.

It is better than Gooch crucible due to following reasons



sintered glass crucible

- No extra preparation is needed
- No filter paper is used. Thus, fibres of filter paper do not make the product impure.
- It can be easily handled
- Reactive materials (e.g. conc. HCl, $KMnO_4$ solution) can be easily filtered.

Difference between filtration through Gooch crucible and Sintered Glass crucible.

	Gooch crucible		Sintered glass crucible
1	It is made of porcelain.	1	It is made of glass.
2	It has a porous base.	2	It has a sintered glass disc sealed into its bottom.
3	Its base is covered with filter paper or asbestos mat.	3	Filter paper or Asbestos mat are not needed.
4	Reactive materials cannot be filtered easily, since they react with filter paper. Therefore, asbestos mat is used to filter such materials.	4	Reactive materials can be filtered easily, since no filter paper is used.
5	Fibres of filter paper or asbestos mat may contaminate the product.	5	Since no filter paper or asbestos mat is used, therefore, no contamination of the product.

CRYSTALLIZATION

The process for obtaining crystals of a substance by cooling its hot saturated solution is called crystallization.

Crystallization is used to purify crude solid product

Principle

Its principle is that

"Solute is highly soluble in a given solvent at high temperature and excess amount of the solute comes out as crystals when this solution is cooled."

Method

It involves following steps

(1) Choice of solvent (2) Preparation of saturated solution (3) Filtration

(4) Cooling (5) Collecting the crystals (6) Drying the crystals

(7) Decolourization of undesirable colour

Exercise Q9:

Write down the main characteristics of a solvent for crystallization of a compound.

(1) Choice of Solvent

The solvent is chosen on hit and trial basis. Many solvents are tried.

Properties (Characteristics) of an Ideal Solvent.

(a) It should dissolve a large amount of solute at its boiling point, and very small amount at room temperature.

(b) It should not react chemically with the solute

(c) It should not dissolve impurities, **or** impurities should not crystallize out along with the solute.

(d) On cooling, it should give well-formed crystals of the pure compound

(e) It should be cheap

(f) It should be safe to use

(g) It should be easily removable

Solvents for Crystallization

- Commonly used solvents for crystallization are: water, rectified spirit (95% ethanol), absolute ethanol, diethyl ether, acetone, chloroform, CCl_4, acetic acid and petroleum ether.
- If no solvent is found suitable, then a combination of two or more solvents is used
- If the solvent is inflammable then heating is done on a water bath.

(2) Preparation of Saturated Solution

- The substance is dissolved in minimum amount of the selected solvent.
- It is then heated directly or on water bath with constant stirring.
- More solvent may be added to the boiling solution until all the solute is dissolved.

(3) Filtration

- The insoluble impurities are removed, by filtering hot saturated solution.
- The solution is filtered hot to avoids premature crystallization of the solute on the filter paper or in the stem of funnel.
- Hot water funnel may be used for this purpose.

(4) Cooling

- Hot filtered solution is cooled at a moderate rate in order to obtain medium sized crystals.
- Slow cooling gives bigger sized crystals, which usually contain solvent with impurities. Such crystals are difficult to dry.

(5) Collecting the Crystals

- When crystallization is complete, the mixture of crystals and mother liquor is filtered through Gooch crucible using a vacuum pump.
- Full suction is applied in order to remove maximum liquor from the crystals.
- If filter cake is hard, it is pressed firmly with a cork to remove remaining mother liquor.
- Crystals are then washed with small amount of cold solvent several times.
- Mother liquor is often concentrated by evaporation. It is then cooled to obtain a fresh new crop of crystals.
- The efficiency of the crystallization process depends upon the percentage of pure material obtained from crude substance.

(6) Drying the Crystallized Substance

There are three methods for drying crystals

(i) Filter Paper:

- Crystals may be dried by pressing between several folds of the filter paper. This method has two disadvantages
  - (a) The crystals are crushed to a fine powder and
  - (b) The fibres of filter paper often contaminate the product.

(ii) Oven:

Drying can be done in an oven if the substance does not melt or decompose on heating.

(iii) Vacuum desiccator:

- Vacuum desiccator is a much better method. In this, crystals are spread on a watch glass and kept in a vacuum dessicator for several times.
- The drying agents used in a dessicator are $CaCl_2$, Silica gel or P_2O_5

(7) Decolourization of Undesirable Colours

- During preparation of a crude substance, sometimes colouring materials or resinous products makes the substance coloured.
- Colouring impurities are removed by boiling the substance in the solvent with animal charcoal.
- This solution is then filtered. The coloured impurities are adsorbed by animal charcoal.
- Pure decolourized substance crystallizes out from the filtrate on cooling.

SUBLIMATION

The process of direct conversion of a solid into vapours by heating without passing through liquid phase is called sublimation.

$$\text{Solid} \rightleftharpoons \text{Vapour}$$

Sublimation is used to purify solid substances.

The substance obtained after sublimation is called sublimate.

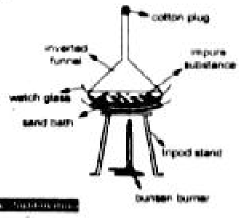
The impure substance, which is sublimed, is called sublimand.

Examples:

iodine, NH_4Cl, naphthalene, anthracene, benzoic acid etc.

Method:

- The impure substance is taken on a watch glass.
- It is covered with an inverted funnel having a cotton plug into its stem.
- The funnel is cooled with wet cotton.
- The substance is heated slowly on a sand bath.
- The pure solid deposits on the inner cold side of the funnel.



DISTRIBUTION LAW OR PARTITION LAW

It states

At constant temperature, a solute distributes itself between two immiscible liquids in a constant ratio of concentration, independent of the amount of solute added.

Applications

This law is helpful in separation and purification of substances from mixtures. Two important techniques are based upon distribution law.

(i) Solvent extraction ***(ii)*** Partition Chromatography.

Distribution Coefficient

At constant temperature, the ratio of concentration of a substance in two immiscible liquids, present in equilibrium with each other, is called distribution co-efficient.

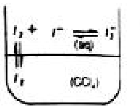
It is denoted by K

Mathematically

$$K = \frac{\text{Concentration of a susbance in organic phase (e.g. } CCl_4)}{\text{Concentration of a substance in aqueous phase (water)}}$$

Example: Distribution of Iodine between CCl_4 and water containing KI

- Consider the distribution of I_2 between two immiscible liquids, CCl_4 and water in the presence of KI.
- Iodine is insoluble in water. When KI is added in water, it ionizes as
  $KI \rightleftharpoons K^+ + I^-$
- Iodine reacts with iodide ion to give tri-iodide ion in a reversible reaction.
  $I_2 + I^- \rightleftharpoons I_3^-$



- Thus, iodine dissolves as I_3^- ion in water (aqueous phase).
- Now if CCl_4 is added to an aq. solution of tri-iodide ion. Iodine is more soluble in CCl_4. So it moves from aqueous layer to the CCl_4 layer (organic layer).
- As a result, brown colour of tri-iodide ion in aqueous layer fades while the purple colour of free iodine appears in CCl_4 layer.
- This system of CCl_4 and H_2O is shaken to increase the area of contact between the layers. Thus, more and more iodine moves from aqueous to organic layer.
- After sometimes, equilibrium is established between the two layers. At this point, the rate of movement of I_2 from H_2O to CCl_4 becomes equal to the rate of movement of I_2 from CCl_4 to H_2O.
- Thus at equilibrium, the ratio of conc. of I_2 in both layers will be constant at constant temperature. This constant is called distribution co-efficient denoted by K and is given by

$$K = \frac{[I_2(CCl_4)]}{[I_2 \text{ as } I_3^-(aq)]}$$

SOLVENT EXTRACTION

The process of obtaining a substance from a solution with the help of an immiscible solvent is called solvent extraction.

Principle

- Solvent extraction is based upon Distribution Law
- A solute can be separated from a solution by an immiscible solvent. The desired solute is more soluble in solvent than solution.
- Thus, solute will move from solution to the added solvent layer. This layer can be separated. The solute can be obtained by evaporating the solvent.

Example: Ether extraction, a commonly used laboratory solvent extraction.

It is mainly used to separate organic compounds from water.

Method

- The aqueous solution containing organic compound is shaken up with ether in a separating funnel.

- The organic compound will move from water layer to the ether layer. The inorganic impurities remain in the aqueous layer.
- The ether layer is separated from separating funnel.
- Ether is then evaporated to get the pure organic compound.
- Repeated extractions using smaller portions of solvent are more effective than using single extraction with larger volume of solvent.
- This technique is particularly useful to obtain the product which is volatile or thermally unstable. Such products are difficult to obtain by other techniques.

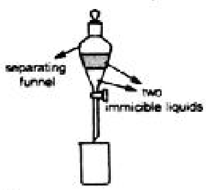


Figure: Separating funnel

CHROMATOGRAPHY

It is an analytical technique used for the separation of a mixture, due to different distribution of substances, between a stationary phase and a mobile phase.

Origin of name

Chromatography is derived from Greek word ***'Khromatos'***, meaning ***'Colour writing'***.

Stationary Phase

It may be a solid or a liquid supported on an inert solid.

Examples: Silica gel, water adsorbed in paper etc.

Mobile Phase

It may be a liquid or a gas. It flows over the stationary phase.

Examples: Ethanol, Acetone, Hexane etc.

Principle

- It is based upon distribution law.
- The mixture is allowed to come in contact with two phases, a stationary phase and a mobile phase. Different components have different affinities for the stationary phase and mobile phase due to which they are separated.
- The distribution of the component between two phases is controlled by distribution coefficient K given as

$$K = \frac{\text{conc. of a component in the mobile phase}}{\text{conc. of a component in the stationary phase}}$$

Hence, Compound with smaller K value remains with stationary phase.

While, Compound with larger K value goes with the mobile phase.

Classes of Chromatography

Chromatography is divided into many classes. Two important classes of chromatography are

(1) Adsorption chromatography

(2) Partition chromatography

Adsorption Chromatography

In this chromatography, stationary phase is a solid.

When mobile phase flows over the stationary phase, substances leave the mobile phase and adsorbed on the stationary phase.

Partition Chromatography

In partition chromatography, stationary phase is a liquid, supported on an inert solid

In this a substance distributes it self between the mobile phase and the stationary phase

For each class of chromatography many methods can be used.

e.g., partition chromatography can be performed by following method.

- Paper Chromatography

Difference between Adsorption and Partition Chromatography

	Adsorption chromatography		Partition chromatography
1	In adsorption chromatography, stationary phase is solid.	1	In partition chromatography, stationary phase is a liquid supported on an inert solid.
2	In this chromatography, solute particles are adsorbed on the solid stationary phase, during their separation.	2	In this chromatography, solute distributes itself between stationary and mobile phase.
3	Example: Thin layer chromatography (T.L.C).	3	Example: Paper chromatography.

Paper Chromatography

It is a method of partition chromatography.

It has

Stationary Phase: A liquid adsorbed on a paper

Mobile Phase: A liquid passing over the adsorbed liquid in paper. It is usually an organic liquid e.g. Ethanol, acetone etc..

Paper chromatography can be done in many ways

(I) Ascending ***(II)*** Descending ***(III)*** Radial/Circular

Ascending paper chromatography is more common.

Ascending Paper Chromatography

In this method, solvent is placed at the bottom of a vessel. A paper is suspended in it. The solvent moves upward by capillary action.

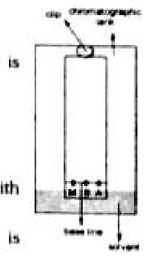


Figure: Paper Chromatography

Procedure

- A solvent mixture is placed in a chromatographic tank.
- The tank is covered with a lid so that its inner space is saturated with solvent vapours and become homogenous.
- About 20 cm strip of Whatmann's Chromatographic paper No. 1 is taken.
- A line is drawn with a thin pencil, about 2.5 cm above from one end of paper. This is the base line.
- A drop of mixture is placed on the base line.

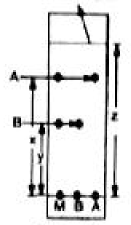
  To identify components, spots of known compounds may also be placed alongside.
- The spots are dried.
- The paper is suspended in the chromatographic tank in such a way that the base line must be above the level of solvent and the paper is dipped to a depth of 5-6mm. This arrangement is left for sufficient time.
  - When solvent front has moved to $\frac{3}{4}$th of the length of the paper, paper is removed from the tank.
- Solvent front is marked with a pencil and paper is dried.

Chromatogram and its development

- The pattern of spots on the dried paper is called chromatogram.
- ***Development:***

  (i) The spots of separated substances can be seen on paper if the substances are coloured.

  (ii) Otherwise, physical or chemical methods are applied on paper to identify spots of substances.



Chromatogram

Retardation Factor

Each component of a mixture has specific value of Retardation Factor or Retention Factor (R_f values).

R_f value is defined as the ratio of the distance travelled by a component from base line to the distance travelled by solvent from base line.

- Mathematically

$$R_f = \frac{\text{Distance travelled by a component from base line}}{\text{Dis tan ce travelled by solvent from base line}}$$

e.g. From the fig.

$$R_f(A) = \frac{x}{z} \quad \text{and} \quad R_f(B) = \frac{y}{z}$$

- R_f value has no unit since it is the ratio of two similar quantities.

Uses of Chromatography

- It is used for the separation and purification of substances from a mixture.
- It is used for qualitative and quantitative analysis.
- It is used to determine the purity of a substance.

OBJECTIVE AND SHORT ANSWER QUESTIONS (Exercise)

Q.1 *Multiple Choice Questions.*

(i) A filtration process could be very time consuming if it were not aided by a gentle suction which is developed:
(a) if the paper covers the funnel up to its circumference.
(b) if the paper has got small sized pores in it.
(c) if the stem of the funnel is large, so that it dips into the filtrate.
(d) if the paper fits tightly.

(ii) During the process of crystallization, the hot saturated solution: *(Rawalpindi Board, 2012)* **2012**
(a) is cooled very slowly to g ' large sized crystals.
(b) is cooled at a moderate rate to get medium sized crystals.
(c) is evaporated to get the crystals of the product.
(d) is mixed with an immiscible liquid to get the pure crystals of the product.

(iii) Solvent extraction is an equilibrium process and it is controlled by.
(a) law of mass action (b) the amount of solvent used
(c) distribution law (d) the amount of solute.
(Faisalabad Board, 2007, 2009) (Bahawalpur Board, 2009) (Sargodha Board, 2009) (D.G. Khan Board, 2009) (Multan Board, 2011) (Lahore Board, 2010) (Rawalpindi Board, 2011) (D.G. Khan Board, 2012)

(iv) Solvent extraction method is a particularly useful technique for separation when the product to be separated is:
(a) non-volatile or thermally unstable.
(b) volatile or thermally stable.
(c) non-volatile or thermally stable.
(d) volatile or thermally unstable.
(D.G. Khan Board, 2012) (Lahore Board, 2013: Gujranwala Board, 2013)

(v) The comparative rates at which the solutes move in paper chromatography, depend on:
(a) the size of paper used.
(b) R_f values of solutes.
(c) temperature of the experiment.
(d) size of the chromatographic tank used.
(Bahawalpur Board, 2008) (Rawalpindi Board, 2009) (Multan Board, 2010) (Sargodha Board, 2012) (Gujranwala Board, 2012) (Gujranwala Board, 2014)

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (d)	(ii) Ans: (b)
If the filter paper does not fit tightly, suction will not be developed.	Slow cooling gives bigger sized crystals, which usually contain solvent with impurities. While fast cooling gives smaller size crystals. Therefore, hot saturated solution is cooled at moderate rate to get medium size crystals.

(iii) Ans: (c)	(v) Ans: (d)
In solvent extraction, solute is distributed between two immiscible liquids. The distribution of solute is controlled by distribution law. It states, At constant T, a solute distributes itself between two immiscible liquids in a constant ratio, independent of the amount of solute added.	In solvent extraction technique, product is not decomposed because no much heating is required.

(v) Ans: (b)

In paper chromatography, the solute moves according to their R_f values.

It is defined as

$$R_f = \frac{\text{Distance travelled by a component from base line}}{\text{Distance travelled by solvent from base line}}$$

Each component has its own R_f value.

Q.2 Fill in the blanks.

(i) A complete chemical characterization of a compound must include _______.

(ii) During filtration, the tip of the stem of the funnel should touch the side of the beaker to avoid _______.

(iii) A fluted filter paper is used to _______ the process of filtration.

(iv) A solvent used for crystallization is required to dissolve _______ of the substance at its boiling point and _______ at the room temperature.

(v) Repeated solvent extractions using small portions of solvent are _______ than using a single extraction with larger volume of the solvent.

Answers:
(i) qualitative and quantitative analysis (ii) splashing
(iii) increase the rate (iv) large amount, small amount (v) more efficient

Q.3 Tick the correct sentences. If the sentence is incorrect, write the correct statements.

(i) A qualitative analysis involves the identification of elements present in a compound.

(ii) If the process of filtration is to run smoothly, the stem of the funnel should remain empty.

Correct Statement If the process of filtration is to run smoothly, the stem of the funnel should remain full of liquid.

(iii) If none of the solvents is found suitable for crystallization a combination of two or more immiscible solvents may be used.

Correct Statement If none of the solvents is found suitable for crystallization a combination of two or more miscible solvents may be used.

(iv) A solute distributes itself between two immiscible liquids in a constant ratio of concentrations depending upon the amount of solvent added.

Correct Statement A solute distributes itself between two immiscible liquids in a constant ratio of concentrations independent of the amount of solute added.

(v) Paper chromatography is a technique of partition chromatography.

Answers:
(i) True (ii) False (iii) False (iv) False (v) True

Q.4 Why is there a need to crystallize the crude product?

*(D.G. Khan Board, **2007**: Faisalabad Board, **2007**: Gujranwala Board, **2010**: Lahore Board, **2014**)*

When a solid substance is produced during a chemical reaction, it always contains impurities. To obtain pure solid compound, crude product is crystallized from a suitable solvent.

Q.5 A water insoluble organic compound aspirin is prepared by the reaction of salicylic acid with a mixture of acetic acid and acetic anhydride. How will you separate the product from the reaction mixture?

During preparation of aspirin, when reaction mixture is thrown in H_2O, aspirin is precipitated. Then it is separated from the reaction mixture by suction filtration. The crude product is then crystallized from a mixed solvent (i.e., solvent containing equal volume of acetic acid and water).

Q.6 A solid organic compound is soluble in water as well as in chloroform. During its preparation, it remains in aqueous layer. Describe a method to obtain it from this layer.

The organic compound can be obtained by solvent extraction technique. In the given conditions, the organic compound is present in aqueous layer.

Since given organic compound is also soluble in chloroform and chloroform is almost immiscible with H_2O. Hence, organic compound can be separated by shaking aqueous layer with chloroform in a separating funnel. The compound goes into the chloroform layer, which is separated from aqueous layer. Then chloroform is evaporated to get pure organic compound.

Q.7 The following figure shows a developed chromatogram on paper with five spots.

(i) Unknown mixture X (ii) Sample A
(iii) Sample B (iv) Sample C
(v) Sample D

Find out

(i) The composition of unknown mixture X

The chromatogram shows that the mixture X contains component B and C

(ii) Which sample is impure and what is its composition

The impure sample is D as it contains A and C.

Q.8 In solvent extraction technique, why repeated extraction using small portions of solvent are more efficient than using a single extraction but larger volume of solvent? (Sargodha Board, 2010: Lahore Board, 2011: Rawalpindi Board, 2008)

Repeated extraction using small portions of solvent are more efficient because more amount of substance is extracted.

Q.9 Write down the main characteristics of a solvent for crystallization of a compound.

Solved on Page 77

Q.10 You have been provided with a mixture containing three inks with different colours. Write down the procedure to separate the mixture with the help of paper chromatography.

Inks can be separated by following method

- A solvent mixture is placed in a chromatographic tank.
- The tank is covered with a lid so that it's inner space is saturated with solvent vapours and become homogenous
- About 20 cm strip of What mann's Chromatographic paper No. 1 is taken.
- A line is drawn with a thin pencil, about 2.5 cm above form one end of paper. This is the base line.
- A drop of mixture of inks is placed on the base line.
- After drying the spots, the paper is suspended in the chromatographic tank and left for sufficient time.
- When solvent front has moved to ¾th of the length of the paper, paper is removed from the tank.
- Solvent front is marked with a pencil line and paper is dried.
- The spots of inks can be seen on paper

For each type of ink R_f values can be calculated by using the formula

$$R_f = \frac{\text{Distance travelled by a particular ink from base line}}{\text{Dis tan ce travelled by the solvent from base line}}$$

HELLO! Mr. Question here!

Multiple Choice Questions from PAST PAPERS

1. Gooch crucible is made of: (Lahore Board, 2014)
   (a) Clay (b) Asbestos (c) Porcelain (d) Iron
2. Solvent extraction is a process: (Lahore Board, 2014)
   (a) Exothermic (b) Endothermic (c) Equilibrium (d) Non-equilibrium
3. Direct conversion of the solid into vapours is called: (Gujranwala Board, 2008, 2010)
   (a) crystallization (b) sublimation (c) distribution (d) vaporization
4. Which one of the following substances is used as decolourizing agent? (Gujranwala Board, 2008, 2009: Multan Board, 2013)
   (a) asbestos (b) conc H_2SO_4 (c) animal charoal (d) silica gel
5. Substance that does not show the process of sublimation is: (Gujranwala Board, 2011)
   (a) $K_2Cr_2O_7$ (b) iodine (c) naphthalene (d) $NH_4C\ell$
6. Insoluble particles can be separate from liquid by: (Multan Board, 2011)
   (a) Sublimation (b) Solvent extraction (c) Filtration (d) Crystallization
7. The drying agent used in a desiccator is (Rawalpindi Board, 2013)
   (a) NaCl (b) KBr (c) $CaCl_2$ (d) $BaCl_2$
8. Which of the following is purified by sublimation: (Lahore Board, 2009)
   (a) Naphthalene (b) Benzoic acid (c) Ammonium Chloride (d) all of these
9. Iodine dissolve in water in the presence of KI due to formation of which one of the following species? (Faisalabad Board, 2010)
   (a) I_2 (b) I (c) I_3^- (d) I_4
10. That chemical analysis in which all the elements present in a compound identified is called: (Faisalabad Board, 2010)
    (a) Quantitive analysis (b) Qualitative analysis
    (c) Gravimetric analysis (d) None of these
11. When hot saturated solution is cooled very rapidly we get. (Rawalpindi Board, 2010)
    (a) medium size crystals (b) large size crystals
    (c) premature crystallization of the substance (d) no crystallization
12. The most common solvent used in solvent extraction is (Faisalabad Board, 2011)
    (a) Acetone (b) Ethanol (c) Rectified spirit (d) Diethyl ether
13. Chromatography in which the stationary phase is liquid is called: (Lahore Board, 2007)
    (a) adsorption chromatography (b) partition chromatography
    (c) column chromatography (d) none of these

14. Which of the following substance shown the property of sublimation? (Sargodha Board, 2010)
(a) NaCl (b) NH_4Cl (c) $CuSO_4$ (d) CH_3COOH
15. In chromatography the stationary phase (D.G. Khan Board, 2010)
(a) is a solid (b) is a liquid
(c) may be liquid or gas (d) may be solid or liquid
16. The substance used as drying agent in desiccator is (Bahawalpur Board, 2010)
(a) Alcohol (b) conc. H_2SO_4 (c) 50% KOH (d) Ether
17. A component having small value of K (distribution coefficient) mostly remains in the (Sargodha Board, 2013)
(a) stationary phase (b) mobile phase (c) chromatographic tank (d) solvent
18. Chromatography in which stationary phase is solid is called (Sargodha Board, 2014)
(a) partition chromatography (b) thin layer chormatography
(c) adsorption chromatography (d) paper chromatography

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(a)	2	(c)	3	(b)	4	(c)	5	(a)
6	(c)	7	(c)	8	(d)	9	(c)	10	(b)
11	(d)	12	(d)	13	(b)	14	(b)	15	(d)
16	(b)	17	(a)	18	(c)				

SHORT QUESTIONS FROM PAST PAPERS: (NO LONG QUESTION)

QUALITATIVE, QUANTITATIVE ANALYSIS

(1) Differentiate between qualitative and quantitative analysis. (Multan Board, 2011)
(2) Give the major steps for the complete quantitative analysis. (Multan Board, 2013)
(3) Name different methods for separation and purification of a compound (D.G. Khan Board, 2008) **OR** Mention various experimental techniques which are used for the purification of substances. (Lahore Board, 2007)

FILTRATION

(1) What do you mean by (a) chromatogram, (b) filtrate (Rawalpindi Board, 2012)
(2) What is filter medium. Name two. (Rawalpindi Board, 2012)
(3) What is meant by filtration and filtration medium (Multan Board, 2012)

(4) Media used for filtration should be selected on the basis of precipitates. Explain. (Lahore Board, 2012)
(5) What should be the size of stem of the funnel used for filtration (Bahawalpur Board, 2008)
(6) How we can run the process of filtration smoothly (Faisalabad Board, 2009)
(7) What is fluted filter paper? Give advantage of its use. (D.G. Khan Board, 2011)
(8) Define filtration. How fluted filter paper is prepared from ordinary filter paper? (Sargodha Board, 2010)
(9) How does Gooch crucible increases the rate of filtration? (Sargodha Board, 2009) **OR** Explain filtration through Gooch crucible. (Rawalpindi Board, 2011)
(10) Differentiate between filtration by Gooch crucible and Sintered glass crucible. (D.G. Khan Board, 2010)
(11) Why sintered glens crucible is preferred to Gooch Cruclble? (Multan Board, 2012)
(12) Concentration HCl and $KMnO_4$ solutions cannot be filtered by using filter paper. Discuss (Gujranwala Board, 2011: Bahawalpur Board, 2011: Faisalabad Board, 2012) **OR** How can HCl and $KMnO_4$ solutions can be filtered by Gooch crucible? (Sargodha Board, 2012)

CRYSTALLIZATION

(1) What is (or Define) crystallization? (Faisalabad Board, 2008: Gujranwala Board, 2008: Sargodha Board, 2012)
(2) Mention the major steps involved in crystallization. (Rawalpindi Board, 2007: Lahore Board, 2007)
(3) Give the main characteristics of the solvent used for crystallization (Lahore Board 2009: Faisalabad Board, 2009: Faisalabad Board, 2010: Multan Board, 2010: Gujranwala Board, 2010: D.G. Khan Board, 2012: D.G. Khan Board, 2012: Azad Kashmir Board, 2012: Bahawalpur Board, 2012: Gujranwala Board, 2012) **OR** Give the salient features of an ideal solvent. (Sargodha Board, 2013) (NOTE: Sometimes two or four characteristics are asked)
(4) Name four (or eight) important solvents chosen for crystallization. (Faisalabad Board, 2007: Rawalpindi Board, 2011: Lahore Board, 2013)
(5) What is disadvantage of slow cooling in crystallization? (Faisalabad Board, 2013)
(6) Describe method to collect crystals from mother liquor (Sargodha Board, 2011)
(7) How vacuum desiccator is used to dry the crystals (Multan Board, 2008: Bahawalpur Board, 2009: Sargodha Board, 2013) **OR** The desiccator is safe and reliable method for drying the crystals. Explain (Lahore Board, 2012)
(8) Name two drying agents used in vacuum desiccator (D.G. Khan Board, 2009) **OR** Name the chemicals which are used as dryig agents in the desiccator? (Multan Board, 2011)
(9) How can you remove undesirable colour from the crystals (Multan Board, 2007: Rawalpindi Board, 2007: Bahawalpur Board, 2008: Gujranwala Board, 2008: Rawalpindi Board, 2010) **OR** How the colouring impurties are removed from a crude substance? (Rawalpindi Board, 2013)

SUBLIMATION

(1) Define sublimation with examples OR What is sublimation? Name any two sublimates (or sublime solids) (Lahore Board, 2008: Rawalpindi Board, 2010: D.G. Khan Board, 2012: Gujranwala Board, 2013: Lahore Board, 2014: Multan Board, 2008: Bahawalpur Board, 2011: Sargodha Board, 2014: Sargodha Board, 2009)
(2) Define sublimand and sublimate. (Lahore Board, 2014)

(3) *Explain the process of sublimation.* **(Faisalabad Board, 2012)**
(4) *How naphthalene can be purified?* **(Gujranwala Board, 2008; Rawalpindi Board, 2009)** OR *Naphthalene can be best purified by sublimation. Why?* **(Rawalpindi Board, 2008)**
(5) *Give the importance of sublimation.* **(Lahore Board, 2013)**
(6) *Why solid iodine sublimes? give reason.* **(Sargodha Board, 2007)**
(7) *Differentiate between sublimation and condensation* **(Multan Board, 2009)**

SOLVENT EXTRACTION, DISTRIBUTION LAW

(1) *What is solvent extraction?* **(Azad Kashmir Board, 2012; Lahore Board, 2008, 2013)** OR *State solvent extraction and give importance.* **(Sargodha Board, 2011)**
(2) *Define distribution law (or Partition law) and how it is helpful in solvent extraction?* **(Lahore Board, 2010; D.G. Khan Board, 2011; Gujranwala Board, 2012; Sargodha Board, 2013; Bahawalpur Board, 2010; D.G. Khan Board, 2012; Gujranwala Board, 2014)**
(3) *What is distribution coefficient? To which technique it is applicable.* **(Gujranwala Board, 2009; D.G. Khan Board, 2010)**
(4) *Iodine is more soluble in water in presence of KI. Discuss.* **(Faisalabad Board, 2011)**

CHROMATOGRAPHY

(1) *Define chromatography and give formula of distribution coefficient.* **(Gujranwala Board, 2011)**
(2) *What is chromatography? Give its two types.* **(D.G. Khan Board, 2007)**
(3) *Define chromatography and explain adsorption chromatography.* **(Multan Board, 2010)**
(4) *OR What is adsorption chromatorgraphy?* **(Bahawalpur Board, 20..**
(5) *Define/Differentiate between adsorption and partition chromatography* **(D.G. Khan Board 2009; Lahore Board, 2011; Multan Board, 2012; Sargodha Board, 2013, 2014; Lahore Board, 2015)**
(6) *Define (a) partition law (or Distribution law) (b) chromatography* **(Multan Board, 2013)**
(7) **2011)**
(8) *Differentiate between stationary and mobile phase* **(Multan Board, 2009; Faisalabad Board 2013; Gujranwala Board, 2014)**
(9) *What do you know about R_f value of a component in paper chromatography?* **(Gujranwala Board, 2013)** OR *What is R_f value? Give its formula.* **(Multan Board, 2007)** OR *What is R_f value? Why it has no units?* **(Lahore Board, 2009; Bahawalpur Board, 2009; Faisalabad Board, 2010; Faisalabad Board, 2011; Multan Board, 2012)**
(10) *Give two applications of paper chromatography* **(Bahawalpur Board, 2012)**
(11) *Define chromatography. Give its uses.* **(Gujranwala Board, 2009; Lahore Board, 2010, 2014; Rawalpindi Board, 2013)**
(12) *R_f value is always less than 1.0. Comment on it.* **(Faisalabad Board, 2008)**
(13) *What is the role of stationary phase in chromatography?* **(Sargodha Board, 2007)**

TEST YOUR SKILLS Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) The choice of filter media depends upon
(a) nature of reactants (b) nature of reaction (c) nature of Precipitates (d) nature of filter paper
(ii) Filtration by a glass funnel and filter paper is very
(a) slow (b) difficult (c) fast (d) accurate
(iii) Gooch crucible is not used to filter the solution of
(a) glucose (b) $KMnO_4$ (c) KOH (d) K_2SO_4
(iv) In crystallization, solvent should dissolve more solute at
(a) freezing temperature. (b) room Temperature
(c) high temperature (d) low temperature.
(v) In solvent extraction solute is separated from solution by using the solvent in which the solute is
(a) more soluble (b) partially soluble
(c) insoluble (d) soluble at high temperature.
(vi) Repeated extraction using small portions of solvent are more
(a) accurate (b) efficient (c) slow (d) rapid
(vii) Solvent extraction is based upon
(a) mass law (b) distribution law (c) avogadro's law (d) volume law
(viii) Which of the following is used as drying agent in vacuum dessicator?
a) Silica gel b) Phosphorus trichloride c) Calcium sulphate d) None
(ix) A component having small value of K (distribution coefficient) mostly remains with
(a) Stationary phase (b) Mobile phase (c) Chromatographic tank (d) None of these
(x) Which of the following substance shows the property of sublimation?
a) Sodium chloride b) ammonium chloride c) Copper sulphate d) acetic acid
(xi) Which separating technique is based upon Distribution Law?
a) crystallization b) sublimation c) solvent extraction d) filtration
(xii) Rate of filtration can be increased using
(a) Desiccators (b) Chromatographic tank (c) Cold finger (d) Suction flask
(xiii) A mixture of inks is separated by paper chromatography due to
a) the amount of solvent taken. b) the different R_f values of the inks.
c) the temperature of the system d) amount of inks used.
(xiv) In which technique a solute distributes between two immiscible liquids?
a) crystallization b) solvent extraction c) Filtrion d) distillation
(xv) The safe method of drying crystals is by using
a) oven b) vaccum desicator c) folds of filter paper d) sunlight
(xvi) Which one of the following substances is used as decolourizing agent?
a) asbestos b) conc H_2SO_4 c) animal charcoal d) silica gel
(xvii) Paper chromatography is a technique of
a) adsorption chromatography b) partition chromatography
c) solvent chromatography d) both (a) and (b)

SUBJECTIVE

Time: 2:10 Hours **Marks: 68**

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question numbers carefully. **(22x 2)=44**

Section – I

Q2. Answer any Eight parts from the followings.
(i) Why is there a need for crystallizing a substance?
(ii) Sintered glass crucible is better than Gooch crucible. Why?

(iii) Differentiate b/w adsorption & partition chromatography.
(iv) What are different methods used to dry crystals?
(v) Write down the uses of chromatography.
(vi) What are the major steps for complete quantitative determination of a sample?
(vii) Name the solvents commonly used in crystallization
(viii) How the undesirable colour can be removed in the process of crystallization.
(ix) Differentiate between qualitative and quantitative analysis
(x) Name the substances that can be purified by the process of sublimation.
(xi) Write down the distribution equation for the distribution of I_2 b/w CCl_4 and H_2O?
(xii) What is analytical chemistry?

Q3. Answer any Eight parts from the followings.
(i) How does Gooch Crucible increases rate of filtration?
(ii) Why fluted filter paper is used?
(iii) Why concentrated HCl and $KMnO_4$ solutions cannot be filtered by Gooch Crucible?
(iv) Write the names of the major steps involved in the crystallization?
(v) What is mother liquor?
(vi) What is the safe and reliable method of drying crystals?
(vii) Why crystallization is used?
(viii) Write down the main characteristics of the solvent used for crystallization?
(ix) Define distribution Law or partition Law?
(x) How the mixture of naphthalene and sand is separated?
(xi) What is ether extraction?
(xii) What is paper chromatography? What are its types?

Q4. Answer any Six parts from the followings.
(i) How R_f value is calculated?
(ii) Define sublimation with an example?
(iii) State solvent extraction and give its importance?
(iv) How filter media is selected for filtration?
(v) How value of distribution coefficient affects the separation of components of a mixture in chromatography
(vi) Why hot filtration is necessary during crystallization?
(vii) What is chromatogram?
(viii) Describe method to collect crystals from mother liquor?
(ix) How iodine is dissolved in water?

Section - II (Attempt any three questions) (8x 3)=24

Q5. (a) Write down five characteristics for an ideal solvent for crystallization? (04)
(b) What is the disadvantage of slow cooling in crystallization? (02)
(c) What is the basic principle of crystallization? (02)

Q6. (a) What is distribution law? Give examples. (04)
(b) Define the following (04)
(i) Sublimation (ii) Chromatography

Q7. (a) What are the important considerations for a good filtration process. (04)
(b) Why repeated extractions using smaller portions of solvent are more beneficial than using single extraction with larger volume of solvent? (02)
(c) How solvent extraction is carried out? (02)

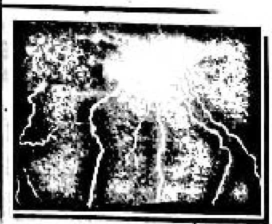
Q8. (a) How many different ways are there to carry out paper chromatography? Briefly describe the procedure for ascending paper chromatograph. (04)
(b) Stem of funnel in filtration should be several inches long. Why? (02)
(c) What type of substances cannot be filtered through Gooch crucible using filter paper? (02)

Q9. (a) What are the common laboratory experimental techniques? (04)
(b) A solid organic compound is soluble in water as well as in chloroform. During its preparation, it remains in aqueous layer. Describe a method to obtain it from this layer. (04)
(b) How will you prepare a fluted filter paper?

Chapter 3

GASES

Avogadro

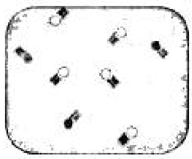


Lightening bolt (Plasma)

Aurora (Plasma)

CONTENTS

Chapter-3 Gases



STATES OF MATTER

Matter exists in four states.

(i) Gas *(ii)* Liquid *(iii)* Solid *(iv)* Plasma

Liquids are less common than solids, gases and plasmas. It is because the liquid state of any substance can exist only within a relatively narrow range of temperature.

Properties of Gases

1. ***Indefinite Volume:*** Gases have indefinite volume. The volume of the gas is equal to the volume of container.
2. ***Indefinite Shape:*** Gases have indefinite shape. They adopt the shape of the container in which they are stored.
3. ***Low density:*** Gases have low densities than solids and liquids. Thus gases bubble through liquids and tend to rise up.
4. ***Joule-Thomson Effect:*** When gases expand suddenly, they cause cooling. This effect is known as Joule-Thomson effect. This effect is used in the liquefaction of gases on industrial scale.
5. ***Effusion & Diffusion:*** Gases can effuse and diffuse.
6. ***Effect of Temperature:*** Gases expand on heating & contract on cooling i.e., increase in temperature increases the volume of gas & vice versa. Liquids and solids do not show considerable increase in volume by increasing temperature.
7. ***Effect of Pressure:*** Gases expand on decreasing pressure and contract on increasing pressure.
8. ***Gas Pressure:*** Gas molecules are in constant random motion. During their motion, they collide with the wall of container. These collisions develop a pressure called Gas Pressure.
9. ***Intermolecular Forces:*** Gases have very weak intermolecular forces.

Properties of Liquids

1. ***Definite volume:*** Liquids have definite volume.

2. ***Indefinite Shape:*** Liquids have <u>indefinite shape</u>. They adopt the shape of the container in which they are stored.
3. ***Constant motion:*** In liquids, molecules are in <u>constant motion</u>. Evaporation and diffusion properties of liquids are due to this motion.
4. ***Densities:*** The <u>densities</u> of liquids are <u>greater</u> than gases and close to solids.
5. ***Intermolecular forces:*** The intermolecular forces among the liquid molecules are <u>stronger</u> than gases but <u>weaker</u> than solids. The melting points and boiling points of liquids depend upon the strength of these forces.
6. ***Spaces:*** The <u>spaces</u> among the liquid molecules are <u>negligible</u> just like solids.
7. ***Kinetic energy:*** Liquid molecules have <u>K.E</u>. Liquids can be converted into solids by cooling i.e. by decreasing the K.E. of the molecules.
8. ***Collisions:*** Molecules of liquids <u>collide</u> with one another and <u>exchange</u> energy.
9. ***Diffusion:*** Liquids can diffuse into other liquids. However, the rate of diffusion is smaller than that of gases.

Properties of solids

1. ***Definite shape:*** Solid have <u>definite shape.</u>
2. ***Definite volume:*** Solid have <u>definite volume</u>.
3. ***Spaces:*** <u>Molecules</u> of solids are very <u>close</u> to each other. They are tightly packed.
4. ***Incompressible:*** Solids are <u>incompressible due to tight packing.</u>
5. ***Intermolecular forces:*** Solids have <u>strongest</u> intermolecular forces.
6. ***Vibrational motion:*** Solid particles only show <u>vibrational motion</u>.
7. ***Diffusion:*** Solids have negligible rate of diffusion.

Pressure and Units of Pressure

Pressure is the force per unit area. i.e. $P = F / A$

- The SI unit of pressure is Nm^{-2} (Pascal). $1Pa = 1Nm^{-2}$.
- The unit pound per square inch (psi) is most commonly used in engineering work.
- The unit millibar (mb) is commonly used by materologists.
- In chemical work, pressure is defined in terms of standard atmospheric pressure.
The pressure of air that can support 760 mmHg column at sea level, is called one amoshphere.
It is the force exerted by 760mm or 76cm long column of mercury on an area of $1cm^2$ at 0°C.

It is the average pressure of atmosphere at sea level. Its symbol is '**atm**'. So, one atmosphere can support 760 mm column of mercury at sea level.

Interconversion of various pressure units

1 atm = 760 torr = 760 mm of Hg = = 101325 Nm^{-2} *= 101325 Pa = 101.325 kPa (kilopascal) = 14.7 pound inch* $^{-2}$ ~~= 1013.25 millibars~~

GAS LAWS

All gases behave uniformly. When pressure and temperature are changed, the volume of gases is changed. The gas laws describe this uniform behaviour of gases.

The relationships between volume of gases and the external conditions like temperature and pressure are called the gas laws.

Exercise Q.4. (a):
What is Boyle's law of gases? Gives its experimental verification.

Boyle's Law

Robert Boyle gave this law in 1662. It states,

At constant temperature, volume of a given mass of gas is inversely proportional to the pressure exerted on it.

Mathematically $V \alpha \frac{1}{P}$ (When 'T' and 'n' are constants)

$$V = \frac{k}{P}$$

or $PV = k$ ____(1)(When 'T' and 'n' are constants)

Eq (1) gives another statement of Boyle's law

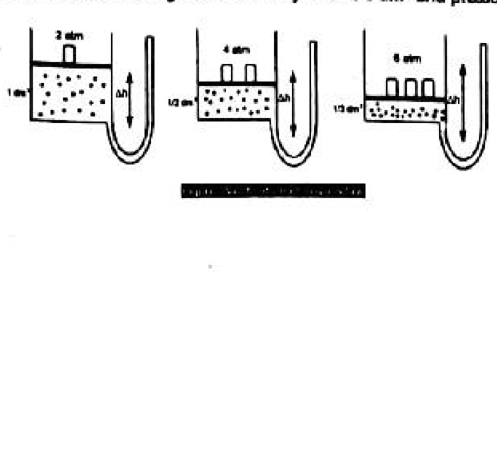
At constant temperature, the product of pressure and volume of a given mass of a gas is always constant.

If the pressure of a given mass of gas is 'P_1' and volume 'V_1', then by changing pressure to 'P_2', volume is changed to 'V_2', such that

So $P_1 V_1 = P_2 V_2$

Experimental Verification of Boyle's Law

- Consider a gas in a cylinder fitted with a movable piston at 25°C. The cylinder is fitted with a manometer to read the pressure of the gas directly.
- Let the initial volume of gas enclosed in cylinder is 1 dm^3 and pressure is 2 atm.



- Then according to Boyle's law
  $P_1V_1 = 2 \times 1 = 2$ atm dm^3 atm= k
- When pressure is doubled on the gas, its volume becomes half.
  Thus P = 4 atm and V = ½ dm^3
  Therefore
  $P_2V_2 = 4 \times ½ = 2$ atm dm^3 = k
- Similarly if pressure is tripled (i.e. 6 atm) on the gas, its volume is reduced to 1/3.
  Therefore
  $P_3V_3 = 6 \times 1/3 = 2$ atm dm^3 = k

Since product of P and V is always constant. Hence Boyle's law is verified.

Example 1:

A gas having a volume of 10 dm³ is enclosed in a vessel at 0°C and the pressure is 2.5 atmospheres. This gas is allowed to expand until the new pressure is 2 atmospheres. What will be the new volume of this gas, if the temperature is maintained at 273 K?

Solution:

$V_1 = 10dm^3$ $V_2 = ?$

$P_1 = 2.5$ atm $P_2 = 2$ atm

Since the temperature is constant ($T_1 = T_2$), thus according to Boyle's law

$$P_1V_1 = P_2V_2$$

$$V_2 = \frac{P_1V_1}{P_2}$$

$$V_2 = \frac{2.5 \text{ atm} \times 10 \text{ dm}^3}{2 \text{ atm}} = \boxed{12.5 \text{ dm}^3}$$

Graphical explanation of Boyle's law

Exercise Q.4. (b):

What are isotherms? What happens to the positions of isotherms when they are plotted at high temperature for a particular gas? (Lahore Board, 2016)

Graph between V and P (Isotherms)

- The plot of volume of a gas on Y-axis and pressure on X-axis at constant temperature (e.g. at 0°C) gives a curve called isotherm.

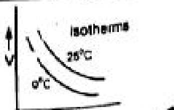


Figure: Isotherms of a gas at different temperatures

- If this graph is plotted at higher constant temperature (e.g., at 25°C), then the curve goes away from both axis. It is

because, at high temperature, the volume of gases is increased.

Similarly, if curve is plotted at further higher temperature, then the curve further goes away from the two axes.

Exercise Q.4. (b):

Why do we get a straight line when pressures exerted on a gas are plotted against inverse of volumes? This straight line changes its position in the graph by varying the temperature. Justify it.

Graph between P and 1/ V

- The plot of pressure (P) on Y-axis against inverse volume (1/ V) of a gas, on X-axis gives a straight line. It is because increase in pressure decreases the volume hence inverse of volume increases. Thus, 'P' is directly proportional to 1/V.

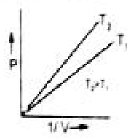


Figure: A plot between P and 1/V

- At higher temperature straight line becomes closer to Y-axis. It is because at higher temperature volume of a gas is increased, therefore, 1 / V is decreased.
- The straight line passes through the origin because when the pressure is close to zero then volume is so high that 1/V is very close to zero.

Graph between PV and P

- A plot of 'P' on X-axis against 'PV' on Y -axis will give a straight line parallel to X- axis. The straight line shows that 'k' is a constant quantity.

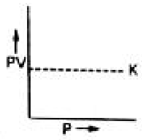


Figure: A plot between pressure and product of PV

- At higher temperature, volume of gas is increased. But new value of PV also remains constant. Thus, a straight line parallel to X-axis is again obtained at higher temperature.
- This straight line helps us to understand the non-ideal behaviour of gases.

Boyle's law is only applicable to ideal gases.

Exercise Q5 (a):

What is the Charles's law? Which scale of temperature is used to verify that V/T = k (pressure and number of moles are constant)?

CHARLES'S LAW

Charles, a French scientist, gave this law in 1787.

It states

At constant pressure, the volume of a fixed mass of gas is directly proportional to the absolute temperature.

Mathematically

$$V \propto T \quad \text{(at constant 'P' and 'n')}$$

$$V = kT$$

$$\frac{V}{T} = k \quad \_\_\_\_ (1)$$

where 'T' is the temperature in Kelvin

Also $$\frac{V_1}{T_1} = \frac{V_2}{T_2} = k$$

Eq. (1) also shows that

At constant pressure, the ratio between the volume of a given mass of a gas and its absolute temperature is always constant.

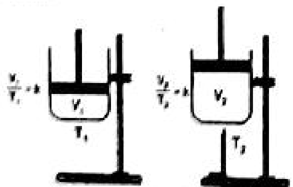
Graph

The graph between 'V' of a given mass of gas and 'T' will be a straight line. It is because, 'V' is directly proportional to the absolute temperature.

[illegible]

Experimental Verification of Charles's Law

- Consider a gas, enclosed in a cylinder fitted with a moveable piston. At temperature T_1, the volume of gas is V_1.
- By increasing the temperature to 'T_2', its volume is increased to 'V_2'. The pressure on the piston is kept constant.



[illegible]

- It is observed that ratio between volume of a given mass of gas and temperature remains constant at constant pressure.

i.e;

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = k$$

Verification of Temperature Scale for Charles's Law

The mathematical form of Charles's law is

$$\frac{V}{T} = K$$

This equation only holds if temperature is on Kelvin scale.

Example:

Consider the following data for a gas when the temperature is on Kelvin scale.

V (dm^3)	1092	846	746
T (K)	546	423	373
V/T ($dm^3 K^{-1}$)	2	2	2

Hence value of $\frac{V}{T}$ is always constant.

However, if temperatrue is taken on Celsius scale, then the above relation is not satisfied. e.g. Consider the following data for above gas when the temperature is on centigrade scale.

V (dm^3)	1092	846	746
T (°C)	273	150	100
V/T ($dm^3\,°C^{-1}$)	4	5.64	7.46

Hence, value of $\frac{V}{T}$ does not remains constant.

Thus, Charles's law is only obeyed if temperature is on Kelvin scale.

Example 2:

250 cm^3 of hydrogen is cooled from 127°C to -27°C by maintaining the pressure constant. Calculate the new volume of the gas at low temperature.

Solution

$V_1 = 250\ cm^3$ $\qquad$ $V_2 = ?$

$T_1 = 127°C + 273 = 400\ K \qquad T_2 = -27°C + 273 = 246\ K$

According to Charles's law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_2 = \frac{V_1 \times T_2}{T_1}$$

$$V_2 = \frac{250 \times 246}{400} = 153.8\ cm^3 = \boxed{0.1538\ dm^3}$$

Exercise Q.6. (a):

What is Kelvin scale of temperature? Plot a graph for one mole of a real gas to prove that a gas becomes liquid, earlier than -273.16°C. ***(Graphical Explanation)***

Absolute Zero

The hypothetical temperature at which the volume of all gases becomes zero is called absolute zero.

Its value is $\underline{-273.16\ °C = 0\ K}$

For routine calculations the value of absolute zero is taken as $-273°C$

Mathematical Explanation: Quantitative statement of Charles's law

At constant pressure, the volume of a given mass of an ideal gas increases or decreases by 1/273 of its original volume at 0°C for every 1°C rise or fall in temperature respectively.

$$\text{Thus Volume at } T°C = V_T = V_0\left(\frac{273 + T}{273}\right) \quad \text{(1)}$$

where V_T = Volume at T°C , T = Temperature in °C

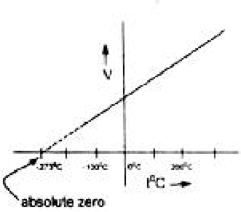
Therefore at $-273°C$

$$V_{-273} = V_0\left(\frac{273 - 273}{273}\right) = 0$$

- The temperature $\underline{-273\ °C}$ is called <u>Absolute Zero of Kelvin scale</u>. Thus volume of a gas becomes zero at absolute zero.
- Absolute zero can never be achieved. It is considered as the lowest temperature. Its value is independent of the nature of gas.
- Charles's law is not obeyed when the temperature is on Centigrade scale. For this reason Kelvin scale was developed with 0 K = -273 °C

Graphical Explanation

- According to Charles's law, when a graph is plotted between '<u>V</u>' and '<u>T</u>' for a gas, a <u>straight line</u> is obtained
- This line intersects the <u>temperature axis at $-273°C$</u>, which is considered as the lowest temperature.
- This temperature is achieved if the substance <u>remains in the gaseous form</u>. But all gases <u>liquefy</u> before reaching this temperature.
- Thus, the lines of all the gases are <u>extrapolated.</u> They meet 'T' axis at -273 °C at which the volume of all gases becomes zero. However, it can never happen for a real gas. Thus, -273 °C is taken as zero of Kelvin scale and it is called absolute zero.
- Generally, <u>greater the mass of the gas greater will be the slope of the line</u>. It is because greater number of moles of gas occupies more volume.



Fig(3.7) The graph between volume and temperature (°C)

SCALES OF THERMOMETRY

The branch of science which deals with the measurement of temperature is called thermometry.

There are three measuring scales of thermometry.

(i) Centrigrade or Celsius Scale *(ii)* Fahrenheit scale *(iii)* Kelvin Scale

(i) Centigrade or Celsius Scale (°C)

The temperature measured on this scales is represented by °C.

On this scale freezing point of water is marked as 0 °C and boiling point as 100 °C. The distance between these two ends is divided into 100 equal parts. Each part is equal to 1 °C.

(ii) Fahrenheit Scale: (°F)

The temperature measured on this scale is represented by °F.

On this scale, the freezing point of water is marked as 32 °F and boiling point as 212 °F . The distance between these two ends is divided into 180 equal parts. Each part is equal to 1 °F.

(iii) Kelvin scale (K)

The temperature measured on this scale is represented by K.

Interconversions of different scales of thermometery

Fahrenheit to Celsius	$°C = \frac{5}{9}(°F - 32)$
Celsius to Fahrenheit	$°F = \frac{9}{5}°C + 32$
Kelvin to Celsius and vice versa	$K = °C + 273.16$

Exercise Q.7. (a):
What is the general gas equation? Derive it in various forms?

GENERAL GAS EUQATION

Derivation

For a given mass of gas, the three variables i.e.; pressure, temperature and volume can be inter-related by one equation known as "General Gas Equation" or "Ideal Gas Equation."

According to Boyles' law

"At constant temperature, volume of a given mass of a gas is inversely proportional to the pressure exerted on it" i.e;

$$V \alpha \frac{1}{P} \quad \text{(at fixed T \& n)} \_\_\_\_ (1)$$

According to Charles' law

"At constant pressure, the volume of a given mass of a gas is directly proportional to the absolute temperature." i.e;

$$V \alpha T \quad \text{(At fixed P \& n)} \_\_\_\_ (2)$$

According to Avogadro's law

"The volume of a gas is directly proportional to the mass (moles) of the gas at constant temperature and pressure i.e;

$$V \alpha n \quad \text{(At fixed T \& P)} \_\_\_\_ (3)$$

Combining eq. (1), (2), (3),

So $$V \alpha \frac{nT}{P}$$

or $$V = \frac{nRT}{P}$$

or $$PV = nRT \_\_\_\_ (4)$$

where *'R'* is constant known as universal gas constant.

Eq. (4) is known as general gas equation.

For 1 mole of a gas

$$PV = RT \quad \text{or} \quad \frac{PV}{T} = R$$

If P,V & T are changed for a gas from P_1,V_1 & T_1 to P_2,V_2 & T_2,

Then $$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

Reduction of General Gas Equation to Boyle's law, Charles's law and Avogadro's law

As $PV = nRT$

If 'T ' and 'n' are constant then PV = k (Boyle's Law)

or $$V = \frac{nRT}{P}$$

If 'P ' and 'n' are constant then V = kT (Charles's Law)

or $$V = \frac{nRT}{P}$$

If 'P ' and 'T ' are constant then V = k n (Avogadro's Law)

Exercise Q7 (b):
Can we determine the molecular mass of an unknown gas if we know the pressure, temperature and volume along with the mass of the gas.

Molecular Mass of Gases

The general gas equation is

$$PV = nRT \_\_\_\_ (1)$$

Since

$$\text{Number of moles} = n = \frac{\textit{Given mass}}{\textit{Molecular mass}} = \frac{m}{M}$$

So equation (1) becomes

$$PV = \frac{m}{M} \times RT \_\_\_\_ (2)$$

or $$M = \frac{mRT}{PV} \_\_\_\_ (3)$$

Thus knowing, pressure (*P*), volume (*V*), temperature (*T*) and mass (*m*) of a gas, its molecular mass (**M**) can be calculated.

Exercise Q7 (c):
How do you justify from general gas equation that increase in temperature or decrease of pressure decreases the density of the gas?

Density of Gases

The general gas equation is

$$PV = nRT \quad \text{\_\_\_\_ (1)}$$

Since $n = \dfrac{\text{Given mass}}{\text{Molecular mass}} = \dfrac{m}{M}$

So eq (4) becomes

$$PV = \frac{m}{M} \times RT \quad \text{\_\_\_\_ (2)}$$

or

$$PM = \frac{m}{V} \times RT \quad \text{\_\_\_\_ (3)}$$

Since, $d = \dfrac{m}{V}$ so eq. (3) becomes

$$PM = dRT$$

$$d = \frac{PM}{RT} \quad \text{\_\_\_\_ (4)}$$

Hence

- Knowing, pressure (*P*), temperature (*T*) and molecular mass (*M*) of gas, its density (*d*) can be calculated.
- The equation shows that density of an ideal gas is directly proportional to its molecular mass and pressure and inversely proportional to the temperature. So, increase in '*M*' and '*P*', increases the density while increases '*T*' increases decreases the density due to increase in volume

IDEAL GAS CONSTANT 'R'

- Numerical value of R is totally independent of the nature of the gas.
- It depends on the units of 'P' and 'V'.
- The value of 'R' is calculated for one mole of a gas at STP using Avogadro's Law.

According to Avogadro's law, At STP one mole of a gas occupies 22.414 dm^3.

Non SI units

At STP

$n = 1.0$ mole $\quad T = 0°C = 273K \quad P = 1.0$ atm

$V = 22.414\ dm^3 \quad R = ?$

$$R = \frac{PV}{nT} = \frac{1 \times 22.414}{1 \times 273}$$

$$\underline{R = 0.0821\ dm^3\ atm\ mol^{-1}\ K^{-1}}$$

or $\quad \underline{R = 62.4\ dm^3\ mm\ of\ Hg\ mol^{-1}\ K^{-1}}$

or $\quad \underline{R = 62.4\ dm^3\ torr\ mol^{-1}\ K^{-1}}$

or $\quad \underline{R = 62400\ cm^3\ torr\ mol^{-1}\ K^{-1}}$

SI units

At STP

$P = 1$ atm $= 101325\ Nm^{-2}$

$T = 273.16$ K

$n = 1.0$ mole

$V = 22.414\ dm^3 = 0.022414\ m^3$

$R = ?$

> Since
> *1 atm = 101,325 Nm^{-2}*
> *$1m^3$ = 1000 dm^3*

$$R = \frac{PV}{nT} = \frac{101325 \times 0.022414}{1 \times 273.16}$$

$\underline{R = 8.3143\ Nm\ mol^{-1}\ K^{-1}}$ or $\underline{R = 8.3143\ J\ mol^{-1}\ K^{-1}}$

Since $\quad$ 1 cal. = 4.18 J

So $\quad R = \dfrac{8.3143}{4.18}\ cal\ K^{-1}\ mol^{-1}$

$$\underline{R = 1.987\ cal\ mol^{-1}\ K^{-1}}$$

Thus unit of 'R' are thus expressed in terms of " energy $mol^{-1}\ K^{-1}$

Physical Significance of value of 'R'

- The value of '***R***' in SI unit is 8.3143 J $mol^{-1}\ K^{-1}$. It shows that if one mole of an ideal gas is present at 273 K and 1 atmospheric pressure and its temperature is increased by 1K, then it will absorb 8.3143 J of energy.
- The value of '***R***' in non-SI unit is 0.0821 dm^3 atm $mol^{-1}\ K^{-1}$. It shows that if one mole of an ideal gas is present at 273 K and 1 atmospheric pressure and its temperature is increased by 1K, then it will absorb 0.0821 dm^3 atm of energy. *(dm^3 atm is the unit of energy)*

Example 8

A sample of nitrogen gas is enclosed in a vessel of volume 380 cm^3 at 120°C pressure of 101325 Nm^{-2}. This gas is transferred to a 10 dm^3 flask and cooled to 27°C. Calculate the pressure in Nm^{-2} exerted by the gas at 27°C. (Gujranwala Board, 2008; Multan Board, 2012)

Solution:

$V_1 = 380\ cm^3 = 0.38\ dm^3$ $\quad V_2 = 10\ dm^3$

$T_1 = 120°C + 273\ K = 393\ K$ $T_2 = 27°C + 273\ K = 300\ K$

$P_1 = 101325\ Nm^{-2}$ $\quad P_2 = ?$

According to general gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\text{Or } P_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{V_2}$$

$$P_2 = \frac{101325 \times 0.38 \times 300}{393 \times 10} = \boxed{2939.2\ Nm^{-2}}$$

Example 4

Calculate the density of CH_4 (g) at 0°C and 1 atmospheric pressure. What will happen to the density if (a) temperature is increased to 27°C, (b) the pressure increased to 2 atmospheres at 0°C.

OR ***Calculate the density of methane at STP.*** (Lahore Board, 2010) **OR** ***Calculate the density of methane at 0°C and 760 mm Hg pressure.*** (D.G. Khan Board, 2011)

Solution:

$T = 0°C + 273\ K = 273\ K$

$P = 1\ atm$

Mol. mass of CH_4 $M = 16\ g\ mol^{-1}$

$R = 0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1}$

$d = ?$

Density is given by the formula

$$d = \frac{PM}{RT}$$

$$d = \frac{1 \times 16}{0.0821 \times 273}$$

$$d = \boxed{0.7139\ g\ dm^{-3}}$$

(a) Density at 27°C

$T = 27 + 273 = 300\ K$

Density is given by the formula

$$d = \frac{PM}{RT}$$

$$d = \frac{1 \times 16}{0.0821 \times 300}$$

$$d = \boxed{0.649\ dm^{-3}}$$

(b) Density at 2 atmospheric pressure and 0°C

$T = 0 + 273 = 273\ K$

$P = 2\ atm$

Density is given by the formula

$$d = \frac{PM}{RT}$$

$$d = \frac{2 \times 16}{0.0821 \times 273}$$

$$d = \boxed{1.427\ dm^{-3}}$$

Example 5

Calculate the mass of 1 dm^3 of NH_3 gas at 30°C and 1000 mm Hg pressure, considering that NH_3 is behaving ideally. (Multan Board, 2012: Lahore Board, 2014)

Solution:

$$P = 1000\ mm\ Hg = \frac{1000}{760}\ atm = 1.316\ atm$$

$V = 1\ dm^3$

$T = 30°C + 273\ K = 303\ K$

Molecular Mass of NH_3 $= M = 17\ g\ mol^{-1}$

Mass of NH_3 $= m = ?$

$R = 0.0821\ dm^3\ atm\ K^{-1}\ mol^{-1}$

Mass of the gas is given by

$$PV = \frac{m}{M}RT$$

$$\text{or} \quad m = \frac{PVM}{RT}$$

$$= \frac{1.316 \times 1 \times 17}{0.0821 \times 300} = \boxed{0.908\ g}$$

Exercise Q.9. (a):

What is Avogadro's law of gases?

AVOGADRO'S LAW

It states

"Equal volumes of all the ideal gases at the same temperature and pressure contain equal number of molecules (or moles)"

So, number of moles of a gas is directly proportional to its volume.

i.e.; $V \propto n$

- It shows that same number of moles of all gases occupies same volume at same temperature & pressure. The volume occupied by ***one mole** of any gas at **STP*** is called ***molar volume*** and is equal to ***22.414 dm^3.***
- One mole of any gas contains constant nnumber of molecules. This number is called Avogadro's number. Its value is 6.02×10^{23}

Examples and Explanation

1 mole of O_2 = 32 g O_2 = 22.414 dm^3 at STP = 6.02×10^{23} molecules of O_2

1mole of H_2 = 2.016 g H_2 = 22.414 dm^3 at STP = 6.02×10^{23} molecules of H_2

So,

1 mole of O_2 and H_2 occupies same volume at STP, although O_2 is 16 times heavier than H_2

It is because molecules in gases are widely separated from one another and have large empty spaces. The distance between two molecules is approximately 300 times the diameter of the molecule. Therefore, size and masses of gas molecules do not affect their volume. Hence, equal moles of all gases occupy same volume at STP.

Facts

- One dm^3 of every gas at STP will have molecules $= \frac{6.02\times10^{23}}{22.414} = 2.68 \times 10^{22}$ molecules

  If temperature and pressure are changed equally for all gases, each gas will have same 2.68×10^{22} molecules.

- One dm^3 of H_2 at STP weighs 0.0899 g. (since $\frac{2.016}{22.414}$ = 0.0899g) and one dm^3 of O_2 at STP weighs 1.4384 g (since $\frac{32}{22.414}$ = 1.4384g) but they contain equal number of molecules (i.e. 2.68×10^{22}).

DALTON'S LAW OF PARTIAL PRESSURE

Dalton's law states,

The total pressure exerted by a mixture of non-reacting gases is equal to the sum of the partial pressures of all the gases present in the mixture.

Mathematical Expression

Let partial pressures of different gases in a mixture are $P_1, P_2, P_3 \ldots$, then according to Dalton's law, total pressure of this mixture is given by

$$P_t = P_1 + P_2 + P_3 + \ldots$$

Partial Pressure

The pressure of each gas in a mixture of gases is called partial pressure of that gas.

Example and Explanation

Consider four cylinders of same volume each.

Three gases H_2, CH_4 and O_2 are enclosed separately in three cylinders at the same temperature.

Let Pressure of H_2 is 400 torr, pressure of CH_4 is 500 torr and pressure of O_2 is 100 torr. Let the three gases are transferred to the fourth cylinder at the same temperature, then according to Dalton's Law total pressure of the mixture of gases will be

$$P_{total} = P_{H_2} + P_{CH_4} + P_{O_2}$$

$$P_{total} = 400+500+100 = 1000 \text{ torr}$$

- Since there are no attractive among the molecules of these gases in a mixture, therefore, every gas exerts its own individual pressure. Hence, total pressure is the sum of individual pressure of these gases.
- Due to independent motion of molecules, general gas equation can be applied to each gas separately.

Thus

$$P_{H_2}V = n_{H_2}RT \quad \text{or} \quad P_{H_2} = n_{H_2}\frac{RT}{V}$$

$$P_{CH_4}V = n_{CH_4}RT \quad \text{or} \quad P_{CH_4} = n_{CH_4}\frac{RT}{V}$$

$$P_{O_2}V = n_{O_2}RT \quad \text{or} \quad P_{O_2} = n_{O_2}\frac{RT}{V}$$

R, T and "V" are constants for all gases in a mixture

Therefore $P_{H_2} \propto n_{H_2}$

$P_{CH_4} \propto n_{CH_4}$

$P_{O_2} \propto n_{O_2}$

Hence, pressure of each gas is directly proportional to its number of moles.

- The total pressure of mixture of gases will be

$$P_t = P_{H_2} + P_{CH_4} + P_{O_2}$$

$$P_t = n_{H_2}\frac{RT}{V} + n_{CH_4}\frac{RT}{V} + n_{O_2}\frac{RT}{V}$$

$$P_t = (n_{H_2} + n_{CH_4} + n_{O_2})\frac{RT}{V}$$

$$P_t = n_t\frac{RT}{V}$$

Where $n_t = n_{H_2} + n_{CH_4} + n_{O_2}$ = total number of all the gases

or $P_t V = n_t RT$

This equation shows that the total pressure of the mixture of gases is directly proportional to the total number of moles of the gases.

Exercise Q10 (b):

Derive an equation to find out the partial pressure of a gas knowing the individual moles of component gases and the total pressure of the mixture.

Calculation of Partial Pressure of a Gas

In a mixture of gases, partial pressure of any gas can be calculated if mass or moles of the gas, total pressure and total number of moles of the gases are known.

Consider two gases A and B forming a mixture of gases.

Let total pressure of the mixture is P_t and number of moles n_t

while Partial pressure of gas A is P_A and number of moles n_A

and Partial pressure of gas B is P_B and number of moles n_B

Then we can write

$P_t V = n_t RT$ ____ (1)

$P_A V = n_A RT$ ____ (2)

$P_B V = n_B RT$ ____ (3)

> **MOLE FRACTION (X)**
> It is the number of moles of a substance divided by total number of moles of all the substances present in the mixture.
> It is denote by X
>
> (see Ch#9, Solutions) for more details.

Divide eq. (2) by (1)

$$\frac{P_A V}{P_t V} = \frac{n_A RT}{n_t RT}$$

$$\frac{P_A}{P_t} = \frac{n_A}{n_t}$$

$$P_A = \frac{n_A}{n_t} \times P_t$$

or

$P_A = X_A \times P_t$ ____ (4)

similarly

$P_B = X_B \times P_t$ ____ (5)

where, X_A and X_B are the mole fractions of gas A and B respectively. Thus, partial pressure of a gas is equal to its mole fraction multiplied by the total pressure.

These equations can be used to determine the partial pressure of the gases in a mixture.

Generally for i^{th} gas in a mixture of gases, we can write $P_i = X_i \times P_t$

Example 6

There is a mixture of hydrogen, helium and methane occupying a vessel of volume 13 dm³ at 37°C and pressure of 1 atmosphere. The mass of H_2 and He are 0.8 and 0.12g respectively. Calculate the partial pressure in mm Hg of each gas in the mixture.

Solution:

Volume of the mixture of gases = V = 13 dm^3

Temperature of the mixture = T = 37°C + 273 = 310 K

Pressure of the mixture = P_t = 1 atm

Total no. of moles = n_t = ?

R = 0.0821 dm^3 atm K^{-1} mol^{-1}

Total number of moles is given by

$$P_t V = n_t RT$$

$$n_t = \frac{P_t V}{RT}$$

$$n_t = \frac{1 \times 13}{0.0821 \times 310} = 0.51 \text{ moles}$$

So, the total number of moles of H_2, He and CH_4 = 0.51 moles

Mass of H_2 = 0.8 g

Molar Mass of H_2 = 2.016 g mol^{-1}

Number of moles of $H_2 = \dfrac{0.8\,g}{2.016\,g\,mol^{-1}} = 0.396$ moles

Mass of He $= 0.12\,g$

Molar Mass of He $= 4\,g\,mol^{-1}$

Number of moles of He $= \dfrac{0.12\,g}{4\,g\,mol^{-1}} = 0.03$ moles

No. of moles of CH_4 = Total moles – (mole of H_2 + moles of He)

$= 0.51 - (0.396 + 0.03)$

$= 0.084$ moles

Mole Fractions can be calculated as

$$x_{H_2} = \frac{\text{No. of oles of } H_2}{\text{Total Number of moles}} = \frac{0.396}{0.51} = 0.776$$

$$x_{He} = \frac{\text{No. of moles of He}}{\text{Total Number of moles}} = \frac{0.03}{0.51} = 0.058$$

$$x_{CH_4} = \frac{\text{No. of moles of } CH_4}{\text{Total Nmber of moles}} = \frac{0.084}{0.51} = 0.164$$

Partial Pressures can be calculated as

$$P_{H_2} = x_{H_2} P$$
$$= 0.776 \times 1.00 = 0.776 \text{ atm}$$
$$= 0.776 \times 760 = \boxed{589.76 \text{ mm Hg}}$$

$$P_{He} = x_{He} P$$
$$= 0.058 \times 1.00 = 0.058 \text{ atm}$$
$$= 0.058 \times 760 = \boxed{44.08 \text{ mm Hg}}$$

$$P_{CH_4} = x_{CH_4} P$$
$$= 0.164 \times 1.00 = 0.164 \text{ atm}$$
$$= 0.164 \times 760 = \boxed{124.64 \text{ mm Hg}}$$

Exercise Q10 (c):

Explain that the process of respiration obeys the Dalton's law partial pressure.

Applications of Dalton's law of Partial Pressure

1. Respiration

Respiration process depends on the difference in partial pressures.

Partial pressure of oxygen in air (159 torr) is greater than in the lungs (116 torr). Therefore, oxygen moves from air into the lungs. The partial pressure of CO_2 in lungs is greater than in the air. Therefore, it moves out from the lungs into the air.

2. Breathing At High Altitude

At sea level, the partial pressure of oxygen in air is 159 torr and breathing is easier. At high altitude, the partial pressure of oxygen is low. It makes breathing difficult. That's why pilots use pressurized cabin during flying.

3. Breathing In Deep Sea

Deep-sea divers cannot breathe with normal air in their tanks. Instead, they use a mixture of an inert gas and O_2 in which partial pressure of oxygen is adjusted around the required limits. Actually, in sea after 100 feet depth, the diver experiences 3 atm pressure. Thus, normal air cannot be breathed in depth of sea. Moreover, the pressure of N_2 increases in depth of sea and it diffuses in the blood.

4. Collection Of Gases Over Water

Gases are usually collected over water. During this process vapours of H_2O are mixed with the gas.

The total pressure (P_{moist}) of this mixture ($H_2O_{vapours}$ + gas) will be

$$P_{moist} = P_g + P_{water\ vapours}$$

The partial pressure of vapours in gases is called aqueous tension.

Thus, $P_{moist} = P_g +$ aqueous tension

or $P_g = P_{moist} -$ aqueous tension

DIFFUSION AND EFFUSION

Diffusion

The spontaneous intermixing of molecules of different gases, due to collision, at a given temperature and pressure is called gaseous diffusion.

Why gases diffuse?

When different gases are mixed together, they wish to have same pressure everywhere. Thus, they go on mixing to form homogenous mixture until their partial pressures become equal everywhere.

Figure: Diffusion

Examples:

- The smell of rose or a scent spreads due to diffusion.
- The mixing of NO_2 (a brown gas) and O_2 (a colourless gas) is also due to gaseous diffusion as shown in the fig. The diffusion occurs by random motion and collision.

Effusion

It is the escape of gas molecules one by one, without collisions through a hole of molecular size, into a region of low pressure.

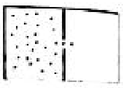


Figure: Effusion

Why gases effuse?

The escape of gas molecules in not due to collision. It is due to their tendency to escape one by one. Gas molecules are habitual in colliding with the walls of vessel.

When a molecule comes in front of a hole, it enters into the other portion of the vessel. This escape is called effusion.

Exercise Q10 (d):

How do you differentiate between diffusion and effusion? Explain Graham's law of diffusion.

Difference between Diffusion and Effusion of gases

	Diffusion		Effusion
1	The spontaneous mixing of molecules of different gases is called diffusion.	1	It is the escape of gas molecules, one by one, without collision, through a hole of molecular size, into a region of low pressure.
2	In this, gas molecules move from an area of its higher concentration to an area of its lower concentration.	2	It is due to the colliding habit of molecules with the wall of the container. During collision, when molecules come in front of a hole, they escape.
3	Gases diffuse by random motion and collision.	3	Gases effuse without collision.
4	Diffusion takes place in all directions.	4	Effusion takes place through a hole of molecular size.
5	Example: The smell of rose or a scent spreads due to diffusion	5	Example: Escape of gas molecules from punctured tyre.

Graham's Law of Diffusion

It was given by an English Scientist, Thomas Graham (1805 – 1869).

The Graham's law states

At constant temperature and pressure, the rate of diffusion (or effusion) of a gas is inversely proportional to the square root of its density or Molecular mass.

Mathematical Expression

$$r \propto \frac{1}{\sqrt{d}} \qquad \text{or} \qquad r \propto \frac{1}{\sqrt{M}}$$

Thus, lighter gases diffuse more rapidly than heavier gases.

Example:

NH_3 gas (molecular mass 17 g mol^{-1}) diffuses more rapidly than HCl gas (molecular mass = 36.5 g mol^{-1})

Explanation

Consider two gases A & B.

For gas 'A' let its rate of diffusion is r_1, density 'd_1', and molecular mass 'M_1'.

For gas 'B' let its rate of diffusion is r_2, density 'd_2', and molecular mass 'M_2'.

Then according to Graham's law

For gas 'A'

$$r_1 \propto \frac{1}{\sqrt{d_1}} \qquad \text{or} \qquad r_1 = \frac{K}{\sqrt{d_1}} \quad \text{------ (1)}$$

For gas B

$$r_2 \propto \frac{1}{\sqrt{d_2}} \qquad \text{or} \qquad r_2 = \frac{K}{\sqrt{d_2}} \quad \text{------ (2)}$$

Constant K is same for all gases at same temperature and pressure.

Dividing (1) by (2), we get

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

Similarly

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Where M_1 and M_2 are molecular masses of gas A and gas B respectively.

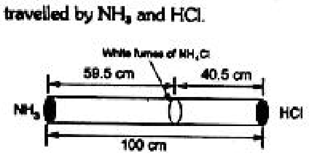
Demonstration of Verification of Graham's Law

Experiment

- Take a 100 cm. long glass tube, opened at both ends.
- Plug a cotton piece, soaked in NH_3 solution at one end and a cotton piece, soaked in HCl solution at other end.
- The vapours of both these gases escape into the glass tube simultaneously.
- The vapours of both NH_3 & HCl are invisible. But when they meet with each other, they produce white fumes of NH_4Cl.

$$NH_3 + HCl \longrightarrow NH_4Cl \text{ (white fumes)}$$

- Determine the distance travelled by NH_3 and HCl.



Calculations

Molecular mass of NH_3 = 17 g mol^{-1}

Molecular mass of HCl = 36.5 g mol^{-1}

According to Graham's Law

$$\frac{r_{NH_3}}{r_{HCl}} = \sqrt{\frac{M_{HCl}}{M_{NH_3}}}$$

Thus $$\frac{59.5}{40.5} = \sqrt{\frac{36.5}{17}}$$

$$1.46 = 1.46$$

Hence, Graham's law is verified

Example 7

250 cm^3 of the sample of hydrogen effuses four times as rapidly as 250 cm^3 of an unknown gas. Calculate the molar mass of unknown gas.

(Gujranwala Board, 2014; Sargodha Board, 2014)

Solution:

Rate of effusion unknown gas $= r_x = 1$

Rate of effusion of H_2 gas $= r_{H_2} = 4$

Molar mass of H_2 gas $= M_{H_2} = 2$ g mol^{-1}

Molar mass of unknown gas $= M_x = ?$

According to Graham's law

$$\frac{r_{H_2}}{r_x} = \sqrt{\frac{M_x}{M_{H_2}}}$$

Taking square on both sides

$$\left(\frac{4}{1}\right)^2 = \left(\sqrt{\frac{M_x}{2}}\right)^2$$

$$\frac{M_x}{2} = \frac{16}{1}$$

$$M_x = 16 \times 2 = \boxed{32 \text{ g mol}^{-1}}$$

KINETIC MOLECULAR THEORY OF GASES

To explain the physical behaviour of gases, a theory has been proposed known as kinetic Molecular Theory of gases.

- Kinetic Molecular Theory was proposed by Bernoulli (1738).
- This theory was used by Clausius (1857) to derive the kinetic equation. He explained all the gas laws with this equation.
- It was further developed by Maxwell, Boltzmann and van der waal.
- Maxwell gave law of distribution of velocities
- Boltzmann studied the distribution of energies among the gas molecules.

The main points of this theory are

1. All gases consist of very small particles called molecules. Gases like He, Ne, Ar have monatomic molecules.
2. The molecules of gases are widely separated form one another, therefore, these have large empty spaces between them.
3. The actual volume of the gas molecules is negligible as compared to the total volume of the gas.
4. There are no attractive forces among the gas molecules. Therefore every gas molecule behaves independently.
5. The average K.E. of gas molecules is directly proportional to the absolute temperature i.e. K.E. α T

6. At the same temperature, molecules of every gas have same average kinetic energy.
7. Gas molecules are in constant random motion. They change their direction only when they collide with one another or with the walls of container.
8. The collisions of gas molecules with one another and with the walls of container are perfectly elastic.
9. The pressure of a gas is due to collisions of gas molecules with the walls of container.
10. The motion given by force of gravity is negligible as compare to the motion given by collisions.

KINETIC EQUATION FOR AN IDEAL GAS

Kinetic Equation

R.J. Clausius derived the relationship for the pressure of an ideal gas known as kinetic equation. It is given as

$$PV = \frac{1}{3} mN\bar{c}^2$$

where

P = Pressure of gas, V = volume of gas, m = mass of one molecule of gas

N = number of molecules of gas in the container, $\bar{c}^2$ = mean square velocity

Mean Square Velocity

Definition

The mean of squares of all the possible velocities is called mean square velocity.

If there are n_1 molecules of a gas with velocity c_1, n_2 with velocity c_2 and so on, then the mean square velocity is given by

$$\text{Mean square velocity} = \bar{c}^2 = \frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 \cdots}{n_1 + n_2 + n_3 \cdots}$$

Where $n_1 + n_2 + n_3 \ldots = N$ = total number of molecules.

Why mean square velocity is used?

Under the given conditions, molecules of a gas do not have same velocities. Actually, different velocities are distributed among the molecules. Therefore, mean square velocity of the molecules is taken.

Root mean square velocity

Definition

The square root of mean square velocity is called root mean square velocity denoted by c_{rms}. The value of c_{rms} has been calculated by using kinetic eq. It is given by

$$c_{rms} = \sqrt{\frac{3RT}{M}}$$

where, M = molecular mass of gas T = Absolute Temperature

This equation shows that higher the temperature greater the velocities of the gas molecules.

EXPLANATION OF GAS LAWS ON THE BASIS OF KINETIC MOLECULAR THEORY

1. Boyle's Law

Kinetic eq. for an ideal gas is

$$PV = \frac{1}{3} mN\bar{c}^2 \quad \text{\_\_\_\_ (1)}$$

According to kinetic molecular theory of gases, the kinetic energy of gas molecules i.e., $\frac{1}{2} mN\bar{c}^2$ is directly proportional to the absolute temperature, 'T'.

$$\frac{1}{2} mN\bar{c}^2 \,\alpha\, T$$

$$\frac{1}{2} mN\bar{c}^2 = KT \quad \text{\_\_\_\_ (2)}$$

Multiply and divide R.H.S. of eq. (1) by 2, we get

$$PV = \frac{2}{2} \times \frac{1}{3} mN\bar{c}^2$$

or

$$PV = \frac{2}{3} \times \left(\frac{1}{2} mN\bar{c}^2\right) \quad \text{\_\_\_\_ (3)}$$

Putting eq. (2) in eq. (3)

$$PV = \frac{2}{3} KT$$

If T = constant

Then PV = k'

This is Boyle's law. It shows that at constant temperature, the volume of a given mass of a gas is inversely proportional to the pressure exerted on it.

2. Charles's Law

Kinetic eq. for an ideal gas is

$$PV = \frac{1}{3} mN\bar{c}^2$$

According to kinetic molecular theory of gases, the average kinetic energy of gas molecules i.e., $\frac{1}{2}mNc^2$ is directly proportional to the absolute temperature, 'T'.

$$\frac{1}{2}mN\bar{c}^2 \propto T$$

$$\frac{1}{2}mN\bar{c}^2 = KT \_\_\_\_ (2)$$

Multiply and divide R.H.S. of eq. (1) 2, we get

$$PV = \frac{2}{2} \times \frac{1}{3}mN\bar{c}^2$$

$$PV = \frac{2}{3} \times \left(\frac{1}{2}mN\bar{c}^2\right) \_\_\_\_ (3)$$

Putting eq. (2) in eq. (3)

$$PV = \frac{2}{3}KT$$

Rearranging, we get

$$V = \frac{2K}{3P} \times T$$

If P = constant then

$$V = K'T$$

$$V \propto T$$

This is Charles's law. It shows that at constant pressure, the volume of a given mass of gas is directly proportional to the absolute temperature.

3. Avogadro's Law

Consider equal volume of two gases under the same conditions of temperature and pressure.

Let For gas 1, mass is m_1, velocity c_1 and number of molecules N_1,

and For gas 2, mass is m_2, velocity c_2 and number of molecules N_2

Kinetic equations for the two gases will be

$$PV = \frac{1}{3}m_1N_1\bar{c}_1^2 \qquad \text{for gas 1}$$

$$PV = \frac{1}{3}m_2N_2\bar{c}_2^2 \qquad \text{for gas 2}$$

Since P & V are same for both gases

Therefore

$$\frac{1}{3}m_1N_1\bar{c}_1^2 = \frac{1}{3}m_2N_2\bar{c}_2^2$$

or

$$m_1N_1\bar{c}_1^2 = m_2N_2\bar{c}_2^2 \_\_\_\_ (1)$$

For both gases, at the same temperature, the average K.E. per molecule is also same.

Thus $(K.E.)_1 = (K.E.)_2$

$$\frac{1}{2}m_1\bar{c}_1^2 = \frac{1}{2}m_2\bar{c}_2^2$$

or

$$m_1\bar{c}_1^2 = m_2\bar{c}_2^2 \_\_\_\_ (2)$$

Dividing eq (1) by (2), we get

$$\frac{m_1N_1\bar{c}_1^2}{m_1\bar{c}_1^2} = \frac{m_2N_2\bar{c}_2^2}{m_2\bar{c}_2^2}$$

$$N_1 = N_2$$

Thus, equal volume of both gases under the same conditions of temperature and pressure, contain equal number of molecules, which is Avogadro's law.

4. Graham's Law of Diffusion

Kinetic equations for the two gases will be

$$PV = \frac{1}{3}mN\bar{c}^2 \_\_\_\_ (1)$$

For 1 mole of gas $N = N_A$ and $N_A m = M$ = Molar mass of gas, therefore

$$PV = \frac{1}{3} M \bar{c}^2$$

$$\bar{c}^2 = \frac{3PV}{M}$$

Taking square root

$$\sqrt{\bar{c}^2} = \sqrt{\frac{3PV}{M}}$$

$$\sqrt{\bar{c}^2} = \sqrt{\frac{3P}{M/V}} = \sqrt{\frac{3P}{d}} \quad \text{since } M/V = d = \text{density}$$

Root mean square velocity is actually the rate of diffusion of gas

Therefore, at constant pressure

$$r = \sqrt{\frac{3P}{d}}$$

$$r \propto \sqrt{\frac{1}{d}}$$

It shows that at constant temperature and pressure, the rate of diffusion (or effusion) of a gas is inversely proportional to the square root of its density, which is the Graham's law.

KINETIC INTERPRETATION OF TEMPERATURE

Consider the kinetic eq

$$PV = \frac{1}{3} mN\bar{c}^2 \text{\_\_\_\_\_} (1)$$

Where

m = mass of one molecule of gas N = number of molecules

$\bar{c}^2$ = mean square velocity P = pressure of gas

V = volume

For one molecule the K.E. due to translational motion is given as

$$E_k = \frac{1}{2} m\bar{c}^2 \text{\_\_\_\_\_} (2)$$

where

E_k = average translational K.E. of molecules

Multiply and divide R.H.S. of eq. (1) by 2, we get

$$PV = \frac{2}{2} \times \frac{1}{3} mN\bar{c}^2$$

$$PV = \frac{2}{3} N \times \left(\frac{1}{2} m\bar{c}^2\right) \text{\_\_\_\_\_} (3)$$

Put eq (2) in (3)

$$PV = \frac{2}{3} \times N E_k$$

Let $N = N_A$ = Avogadro's Number

$$PV = \frac{2}{3} \times N_A E_k \text{\_\_\_\_\_} (4)$$

According to general gas equation for 1 mole of a gas

$$PV = RT \text{\_\_\_\_\_} (5)$$

Compare (4) and (5)

$$\frac{2}{3} \times N_A E_k = RT$$

or $$E_k = \frac{3R}{2N_A} \times T$$

Thus there is a direct relationship between translational K.E. and absolute temperature.

Conclusions

- The temperature of a gas is directly proportional to the average translational K.E. of its molecules.

  Thus, a change in temperature changes the motion of molecules of a gas
- The process of heat transfer from hot body to cold body is due to collisions of molecules with each other. During collisions, hot molecules transfer their K.E. to colder molecules until the average translational K.E. of the two bodies become equal. Thus, the T of two bodies becomes equal.
- When $T = 0$ then $E_k = 0$ i.e. motion of molecules stops, which is not possible. This temperature is called absolute zero. It can never be achieved. The lowest temperature attained so far is 10^{-8} K.
- In gases and liquids, temperature is the measure of average translational K.E. but in solids, it is the measure of only vibrational K.E.

LIQUEFACTION OF GASES

General Principle of Liquefaction

The conversions of gases into liquids require high pressure and low temperature

- High P brings the molecules close to each other
- Low temperature decreases the K.E. of molecules. Thus, attractive forces are developed among them and gas is converted into liquid.

Critical Temperature

The highest temperature at which a substance can exist as a liquid is called critical temperature.

It is denoted by T_c

Critical Pressure

The minimum pressure required to liquefy the gas at the critical temperature is called the Critical pressure

It is denoted by P_c

Critical Volume

The volume occupied by one mole of gas at T_c and P_c is called Critical Volume.

It is denoted by V_c

Example:

- For CO_2 $T_c = 31.1°C$, $P_c = 72.9$ atm, $V_c = 95.65\ cm^3\ mol^{-1}$

Importance of critical temperature

- For every gas, there is certain temperature above which a gas cannot be liquefied. This temperature is called critical temperature.

  Examples: T_c for O_2 is 154.4 K (-118.75°C). Similarly, T_c for CO_2 is 31.1°C. So, these gases can be liquefied only below their T_c. Hence, these must be cooled below their T_c and then pressure is applied to liquefy them.

Effect of Polarizability on critical temperature

- Non polar gases have low polarizability and have a very low T_c e.g. T_c of Ar is 150.9 K (-122.26 °C).
- Polar gases have high polarizability and comparatively high T_c e.g. T_c of NH_3 is 405.6 K (132.44°C).
- Thus, polar gases are easily converted into liquids.

Table 3.2 Critical Temperatures and Critical Pressures of some Substances

Substance	Critical Temperature T_c (K)	Critical Pressure P_c (atm)
Water vapours, H_2O	647.6 (374.44 °C)	217.0
Ammonia, NH_3	405.6 (132.44 °C)	111.5
Freon-12, CCl_2F_2	384.7 (111.54 °C)	39.6
Carbon dioxide, CO_2	304.3 (31.142 °C)	73.0
Oxygen, O_2	154.4 (−118.75 °C)	49.7
Argon, Ar	150.9 (−122.26 °C)	48
Nitrogen, N_2	126.1 (−147.06 °C)	33.5

Methods for Liquefaction of Gases

Various methods are used for the liquefaction of gases. These methods are generally based upon Joule Thomson effect.

Joule Thomson Effect

When a compressed gas is allowed to expand suddenly. It produces cooling. This is called Joule - Thomson effect.

Reason: In a compressed gas, molecules are very close to each other and have attractive forces. When a gas is expanded suddenly molecules move away from each other. This process requires energy, which is obtained from the gas itself, hence it is cooled.

Linde's Method

- It is based upon Joule Thomson effect.
- Lind liquefied air by this process.
- The compressed air (about at 200 atm) is passed through a water-cooled pipe where the heat of compression is removed.
- This compressed air is then passed through a spiral tube having a jet at the end. When the gas comes out of jet into low pressure area (1 atm) , it suddenly expands and is cooled due to Joule- Thomson effect.

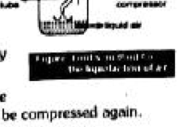


Figure: Linde's method for the liquefaction of air

- The cooled air moves up, cools the incoming gas of the Jet, and then again enters into the compression pump, to be compressed again.
- By repeating compression and expansion again and again, air is liquefied.
- All gases except H_2 and He can be liquefied by this process.

Exercise Q.13. (a):

Gases show non-ideal behaviour at low temperature and high pressure. Explain this with the help of a graph.

NON-IDEAL BEHAVIOUR OF GASES

Definitions:

The gas which obeys gas laws under all conditions of temperature and pressure is called an "Ideal Gas."

While

The gas which does not obey gas laws under all conditions of temperature and pressure is called a "Real Gas" or a "Non-Ideal Gas"

Compressibility factor

The effect of temperature and pressure on behaviour of gases can be studied in terms of a compressibility factor, Such that for 1 mole of a gas

$PV = nRT$

or $\frac{PV}{nRT}$ = compressibility factor

Behaviour of Ideal gas

Since for an ideal gas,

$$PV = nRT.$$

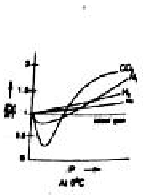
or $\frac{PV}{nRT} = 1$.

Thus value of compressibility factor is '1', for an ideal gas at all temperature and pressure.

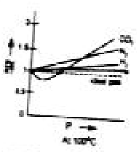
Thus, for an ideal gas, when a graph is plotted between $\frac{PV}{nRT}$ on Y-axis and P on X-axis, a <u>straight line</u> is obtained <u>parallel to pressure axis</u>.

Behaviour of Real gases

Effect of Pressure:



- For He, at low pressure, the curve starts somewhat along the ideal line. However, at very high P, value of $\frac{PV}{nRT}$ has increased from the expected value and He show deviation from ideal behaviour.
- For H_2, deviation starts even at low pressure as compare to He



- For N_2, $\frac{PV}{nRT}$ first decreases below ideal line and then increases
- CO_2 also shows unusual behaviour.

Thus, it shows that deviations depend upon the nature of gas.

Effect of Temperature:

At high temperature, the graph of these real gases come closer to the ideal line. Thus, the gases become ideal.

Hence

Conditions for Ideal and Non-Ideal behaviour of gases

- Gases are <u>non-ideal</u> at <u>high pressure</u> and <u>low temperature</u>.
- Gases are <u>ideal</u> at <u>low pressure</u> and <u>high temperature</u>.

	Ideal Gas		Non-ideal gas
1	It obeys gas laws under all conditions of temperature and pressure	1	It does not obey gas laws under conditions of temperature and pressure
2	There are no attractive or repulsive forces among the gas particles	2	There are attractive and repulsive forces among the gas particles particularly at low T & high P.
3	Actual volume of gas particles is negligible as compered to the total volume of the gas.	3	Actual volume of gas particles is not negligible as compared to the total volume of gas particularly at low 'T' & high 'P'.
4	For an ideal gas $\frac{PV}{RT}$ = constant	4	For an Ideal gas $\frac{PV}{RT}$ = constant
5	It is an imaginary gas and does not exist in nature.	5	It is a real gas and exists in nature. e.g. SO_2, NH_3 etc.

Exercise Q.13. (b):

Do you think that some of the postulates of kinetic molecular theory of gases are faulty? Point out these postulates.

Causes for Deviations from Ideality

Van der Waal (1873) pointed out that two ideal assumptions in the kinetic molecular theory are responsible for these deviations.

(i) The actual volume of the gas particles is negligible as compared to the total volume of gas.

(ii) There are no attractive forces among the gas particles.

At high pressure and low temperature, gas molecules come closer to each other and develop attractive forces among them. Moreover, at high pressure volume of a gas does not remain negligible. So, the behaviour of real gases is not according to kinetic molecular theory of gases and PV=nRT. Thus gases show deviations from ideal behaviour at low temperature and high pressure.

Exercise Q.14 (a):

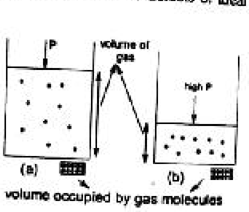
Derive van der Waal's equation for real gases.

van der Waal's Equation for Real Gases

van der Waal made volume and pressure correction to remove the defects of ideal gas model, and gave an equation of state for real gases

Volume Correction

Van der Waal pointed out that gas molecules have definite volume. Although volume of gas molecules is very small as compare to vessel but it is not negligible. Thus, when pressure is increased on gas molecules, they oppose it. So, if V_{vessel} is the total volume of gas and '*b*' is the volume of gas molecules per mole (excluded volume), then the volume available for compression will be $(V_{vessel} - b)$ and not V.



Hence $V_{free} = V_{vessel} - b$ _____ (1)

Thus V_{free} is the volume available to gas molecules.

Where constant ' b' is the characteristic of each gas. Its value is

$b = 4V_m$ where V_m is the molar volume

'*b*' is the effective volume or excluded volume. It is the volume occupied by gas molecules in highly compressed state but not in liquid state.

Pressure Correction

A molecule in the interior of gas has no unbalanced force. It is because it is attracted equally from all sides. However, a molecule just striking the wall of the vessel is more attracted inward. Therefore, it will not strike the wall with full force and hence observed pressure '*P*' will be less than the ideal pressure 'P_i' by an amount P'.

i.e. $P = P_i - P'$

or $P_i = P + P'$ ___ (2)

Consider two types of molecules 'A' and 'B'. Let molecule of type 'A' strikes the wall then it will be attracted inward by molecules of type 'B'. Therefore, P' depends upon the forces of attractions between 'A' and 'B'. Hence net force of attraction is proportional to the concentrations of A type and B type molecules.

i.e. $P' \propto C_A \cdot C_B$ ____ (3)

Let '*n*' is number of moles of A an B present in a total volume '*V*', then concentrations of A and B will be given by

$$C_A = \frac{n}{V} \quad \text{and} \quad C_B = \frac{n}{V} \text{ \_\_\_\_ (4)}$$

Put eq (4) in eq (3)

$$P' \propto \frac{n}{V} \cdot \frac{n}{V}$$

$$P' \propto \frac{n^2}{V^2}$$

$$P' = \frac{a n^2}{V^2}$$

For 1 mole of a gas

$$P' = \frac{a}{V^2} \text{ \_\_\_\_\_ (5)}$$

Where *a* = co-efficient of attraction or attraction per unit volume

For gases with strong intermolecular forces value of '*a*' is high.

Put eq (5) in eq (2)

$$P_i = P + \frac{a}{V^2} \text{ \_\_\_\_\_ (6)}$$

Thus, ideal gas equation for 1 mole will become

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

This equation is called van der Waal's equation of state. This equation is applicable to real gases.

For '*n*' mole of a gas $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

Examples:

- For H_2 gas b = 0.0266 $dm^3\ mol^{-1}$. It means 1 mole of H_2 gas (2.016 g) occupies 0.0266 dm^3 at closet approach in gaseous state.
- For H_2 gas 'a' is the least (0.245) due to its non-polar character and small size.

Units of van der Waals constants 'a' and 'b'

- ***SI units***

  Units of b: $m^3\ mol^{-1}$

  Units of a:

$$a = \frac{P'V^2}{n^2} = \frac{N\,m^{-2}(m^3)^2}{mol^2} = \frac{N\,m^{-2}\,m^6}{mol^2} = N\,m^4\,mol^{-2}$$

- ***Non-SI units***

  Units of b: $dm^3\ mol^{-1}$

  Units of a:

$$a = \frac{P'V^2}{n^2} = \frac{atm\,(dm^3)^2}{mol^2} = atm\,dm^6\,mol^{-2}$$

- The value of 'a' and 'b' can be determined by noting P , V and T under two different conditions.
-

[illegible]

[illegible]	[illegible]	[illegible]
Hydrogen	0.245	0.0266
Oxygen	1.360	0.0318
Nitrogen	1.390	0.0391
Carbon dioxide	3.590	0.0428
Ammonia	4.170	0.0371
Sulphur dioxide	6.170	0.0564
Chlorine	6.439	0.0562

Example 8:

One mole of methane gas is maintained at 300 K. Its volume is 250 cm^3. Calculate the pressure exerted by the gas under the following conditions.

(i) When the gas is ideal

(ii) When the gas is non-ideal

a = 2.253 atm $dm^6\ mol^{-2}$, b = 0.0428 $dm^3\ mol^{-1}$.

(Sargodha Board, **2012**: Gujranwala Board, **2012**: Lahore Board, **2014**)

Solution:

(i) ***When the gas is ideal, general gas equation is applied***

P = ?

V = 250 cm^3 = 0.25 dm^3

n = 1 mole

T = 300 K

R = 0.0821 dm^3 atm $K^{-1}\ mol^{-1}$.

According to general gas eq.

$$P = \frac{nRT}{V}$$

$$P = \frac{1 \times 0.0821 \times 300}{0.25}$$

$$P = \boxed{98.5\ atm}$$

(ii) When the gas is behaving as non-ideal, we should use the van der Waal's equation.

P=?

n = 1 mole

R = 0.0821 dm^3 atm K^{-1} $mole^{-1}$.

V = 0.25 dm^3

T = 300 K

a= 2.253 atm $dm^6\ mol^{-2}$

b = 0.0428 $dm^3\ mol^{-1}$

According to van der Waal's equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\text{or}\quad \left(P + \frac{an^2}{V^2}\right) = \frac{nRT}{(V - nb)}$$

$$\text{or}\quad P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

Putting values

$$P = \frac{1 \times 0.0821 \times 300}{0.25 - 1(0.0428)} - \frac{2.253 \times 1^2}{(0.25)^2}$$

$$P = \frac{24.63}{0.207} - \frac{2.253}{0.0625}$$

$$P = 118.99 - 36.05$$

$$P = \boxed{82.94\ atm}$$

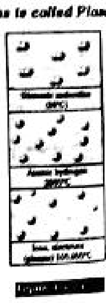
Thus pressure lessened from ideal behaviour = 98.5–82.94 = 15.56 atm

PLASMA STATE

A mixture of neutral particles, positive ions and negative electrons is called Plasma.

Formation of Plasma

- On heating a solid, it is converted into liquid. On further heating, the liquid is converted into vapours. Thus, the phase of matter changes from solid to liquid and then liquid to vapours.
- Now if vapours are further heated some of them lose electrons and positive ions are formed. Hence a mixture of neutral particles, positive ions and negative electrons are produced. This is called Plasma.
- The ionization is produced by high temperature or by radiations.



Occurrence of Plasma or Where Plasma Found

1. About 99% of the universe is made up of Plasma.
2. It is present everywhere in sun and stars
3. The sun is a 1.5 million km ball of plasma. It is heated by nuclear fusion.
4. It is the most abundant form of matter. It is the stuff of stars
5. It is present in everything from sun to quarks (quark is the smallest particle of universe)
6. Majority of the matter in inter-stellar space is plasma
7. All the shining stars are plasma
8. On earth, it is very limited. It is found in lightening bolts, flames, auroras and fluorescent lights, neon signs etc.
9. When an electric current is passed through neon gas, it produces both plasma and light

Characteristics of Plasma

1. It consists of a significant number of charge particles. Thus it respond to both electric and magnetic fields
2. Motion of particles in the plasma produces fields and electric current within plasma density. It refers to the density of charged particles.
3. Plasma has a complex set of interactions. It is a unique fascinating and complex state of matter.
4. It is macroscopically neutral. Although it contains ions and electrons but their number is equal.

Natural and Artificial Plasma

Artificial Plasma

- It is produced by using electrical charges on a gas e.g. in neon signs
- Plasma at low T is hard to maintain. It is because outside a vacuum, low T plasma reacts rapidly with any molecule. Thus, it is both useful and hard to use.

Natural Plasma

- It only exists at high temperature or low temperature vacuums. It does not break down or react rapidly
- These are extremely hot (over 20,000°C minimum)
- They have so much energy, that they can vaporize any material.

Applications

Since plasma can respond to both electric and magnetic fields, it can have many uses

1. A fluorescent bulb is different from regular light bulbs. It consists of a long tube filled with gas. When electricity is passed through gas, it charges up the gas. The charging and exciting of gas creates glowing plasma inside the bulb.
2. Neon signs are glass tube filled with gas. When electricity is passed through the tube, it charges the gas and creates glowing plasma inside the tube. The colour of plasma depends upon the gas used.
3. They are used for plasma processing of semiconductors, sterilization of some medical products, lamps, lasers, diamond coated films, high power microwave sources and pulsed power switches.
4. They are helpful for generation of electricity from fusion pollution control and removal of hazardous chemicals. Thus, it helps to clean up the environment.
5. Plasma light up our offices, homes. It helps in working of computers, electronic equipment.
6. It drives lasers and particle accelerators.
7. It can be used to pasteurize food.
8. It is used to make corrosion resistant tools.

Future Horizons

Scientists are working to use plasma effectively

For effective use

- it should have low energy
- It should survive for sufficient time without reacting and degeneration.

The applications of magnetic field involve the use of plasma. The magnetic fields create low energy plasma, which create metastable state of molecules. These will then react with another molecule with right energy. Thus these molecules can survive long enough to react with desired molecules. These metastable particles are selective in their reactivity. Thus, these can be used to solve problems like radioactive contamination.

Scientists are working on mixture of gases to use as metastable agents on plutonium and uranium.

OBJECTIVE AND SHORT ANSWER QUESTIONS (Exercise)

Q.1. Multiple-choice questions.

(i) Pressure remaining constant, at which temperature the volume of a gas will become twice of what it is at 0°C.

(a) 546°C (b) 200°C (c) 546 K (d) 273K

(Bahawalpur Board, 2009) 2011 B (D.G. Khan Board, 2012) (Sargodha Board, 2012) (Gujranwala board, 2010, 2013, 2014)

(ii) Number of molecules in one litre of water is close to:

(a) $\frac{6.02}{22.4}\times 10^{23}$ (b) $\frac{12.04}{22.4}\times 10^{23}$ (c) $\frac{18}{22.4}\times 10^{23}$ (d) $55.6 \times 6.02 \times 10^{23}$

(D.G. Khan Board, 2010) (D.G. Khan Board, 2012) (Rawalpindi board, 2012) (Lahore board, 2013) (Gujranwala board, 2012)

(iii) Which of the following will have the same number of molecules at STP?

(a) 280 cm^3 of CO_2 and 280 cm^3 of N_2O (b) 11.2 cm^3 of O_2 and 32 of g O_2

(c) 44g of CO_2 and 11.2 dm^3 of CO (d) 28g of N_2 and 5.6 dm^3 of Oxygen

(Faisalabad Board, 2008)

(iv) If absolute temperature of a gas is doubled and the pressure is reduced to one half, the volume of the gas will

(a) remain unchanged (b) increase four times

(c) reduce to ¼ (d) be doubled

(Rawalpindi Board, 2010) (Multan Board, 2011, 2012)

(v) How should the conditions be changed to prevent the volume of a given gas from expanding when its mass is increased?

(a) Temperature is lowered and pressure is increased

(b) Temperature is increased and pressure is lowered

(c) Temperature and pressure both are lowered

(d) Temperature and pressure both are increased

(vi) The molar volume of CO_2 is maximum at

(a) STP (b) 127°C and 1 atm

(c) 0°C and 2 atm (d) 273°C and 2 atm

(D.G. Khan Board, 2009) (Rawalpindi Board, 2009) (Lahore Board, 2010) (Sargodha Board, 2010, 2012, 2013, 2014) (Gujranwala board, 2014)

(vii) The order of the rate of diffusion of gases NH_3, SO_2, Cl_2 and CO_2 is:

(a) $NH_3 > SO_2 > Cl_2 > CO_2$ (b) $NH_3 > CO_2 > SO_2 > Cl_2$

(c) $Cl_2 > SO_2 > CO_2 > NH_3$ (d) $NH_3 > CO_2 > Cl_2 > SO_2$

(Faisalabad Board, 2007, 2008) (D.G. Khan Board, 2012) (Gujranwala board, 2009)

(viii) Equal masses of methane and oxygen are mixed in an empty container at 25°C. The fraction of total pressure exerted by oxygen is

(a) 1/3 (b) 8/9 (c) 1/9 (d) 16/17

(Multan Board, 2010) (Rawalpindi board, 2012) (Gujranwala board, 2012)

(ix) Gases deviate from ideal behaviour at high pressure. Which of the following is correct for non-ideality?

(a) At high pressure, the gas molecules move in one direction only
(b) At high pressure, the collision between the gas molecules are increased manifold
(c) At high pressure, the volume of the gas becomes insignificant
(d) At high pressure, the intermolecular attraction become significant

(x) The deviation of a gas from ideal behaviour is maximum at

(a) $-10^{\circ}C$ and 5.0 atm (b) $-10^{\circ}C$ and 2.0 atm
(c) $100^{\circ}C$ and 2 atm (d) $0^{\circ}C$ and 2 atm

(Lahore Board, 2008, D.G. Khan Board, 2012, Multan Board, 2012)

(xi) A real gas obeying van der Walls equation will resemble ideal gas if

(a) both a and b are large (b) both a and b are small
(c) a is small and b is large (d) a is large and b is small

(Bahawalpur Board, 2010)

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c)
Let
$V_1 = 1$ $T_1 = 0^{\circ}C + 273 = 273$ K
To double the volume
$V_2 = 2$ $T_2 = ?$
According to Charles's law,
$T_2 = \frac{V_2 \times T_1}{V_1} = \frac{2 \times 273}{1} = 546$ K

(ii) Ans: (d)
Mass of 1 dm^3 of water = 1 kg = 1000 g
Molecular mass of water = 18 g mol^{-1}
Moles of water = $\frac{1000}{18}$ = 55.55 moles
1 mole of water contains = 6.02×10^{23} molecules
55.55 moles will contain = $55.55 \times 6.02 \times 10^{23}$ Molecules

(iii) Ans: (a)
Avogadro's law states
"Equal volumes of all gases at the same temperature and pressure contain equal number of molecules"
Since CO_2 and NH_3 have same volume at STP, therefore, they will have same number of molecules.

(iv) Ans: (a)
According to gas laws, volume is directly proportional to T, and inversely proportional to P
i.e. $V \propto \frac{T}{P}$
Thus if 'T' is doubled and 'P' is reduced to one-half, then volume will increase four times
$V \propto \frac{2}{1/2} = 4$

(v) Ans: (a)
Increase in mass of gas increases the volume of gas. Therefore, to keep volume constant, pressure must be increased or temperature must be decreased or both.

(vi) Ans: (b)
Since $V \propto \frac{T}{P}$
In (c) and (d), pressure is high, therefore, volume will be less
In (a) and (b), pressure is low, but in (b) temperature is also high. Hence molar volume of CO_2 will be maximum in (b).

(vii) Ans: (b)
According to Graham's law, rate of diffusion of a gas is inversely proportional to the square root of its molecular mass
i.e. $r \propto \frac{1}{\sqrt{M}}$
Since Molecular masses of NH_3, SO_2, Cl_2 and CO_2 are

(viii) Ans: (c)
According to Dalton's law of partial pressure, partial pressure of a gas in a mixture of gases is directly proportional to its mole fraction. $P_a \propto x_a$
Let equal masses of CH_4 and O_2 are 32 g each. Thus it will be 2 moles of CH_4 and 1 moles of O_2

in the order, $Cl_2 > SO_2 > CO_2 > NH_3$
Therefore, their rate of diffusion will be in the inverse order i.e., $NH_3 > CO_2 > SO_2 > Cl_2$

Hence mole fraction of $O_2 = \frac{1}{3}$, and
mole fraction of $CH_4 = \frac{2}{3}$
Since mole fraction of O_2 is 1/3, therefore, its pressure will also be 1/3 of total pressure

(ix) Ans: (d)
At high P, molecules of gas come closer together. Therefore, they form intermolecular forces. Hence, gas show deviations from ideal behaviour

(x) Ans: (a)
Gases show deviations from ideal behaviour at low temperature and high pressure.
In (a) temperature is lowest and pressure is highest than in (b), (c) and (d).

(xi) Ans: (b)
'a' measures attraction among the gas molecules. Larger 'a', greater attractions
'b' measures volume occupied by gas molecules. Larger 'b', greater volume occupied
For a gas to behave as an ideal gas volume of gas molecules should be negligible and there should be no forces of attractions among gas molecules. Hence, 'a' and 'b' should be small

Q.2. Fill in the blanks

(i) The product PV has the S.I. unit of ______.
(ii) Eight grams each of O_2 and H_2 at $27^{\circ}C$ will have total KE in the ratio of ______.
(iii) Smell of cooking gas during leakage from gas cylinder is detected because of the property of ______.
(iv) Equal ______ of ideal gases at the same temperature and pressure contain ______ number of molecules.
(v) The temperature above, which a substance exists only as a gas, is called ______.

Answers:
(i) Nm (ii) 1:16 (iii) diffusion (iv) volume, equal (v) critical temperature

Q.3. Label the following sentences as true or false.

(i) KE of molecules is zero at $0^{\circ}C$.
(ii) A gas in a closed container will exert much higher pressure at the bottom due to gravity than at the top.
(iii) Real gases show ideal gas behaviour at low pressure and high temperature.
(iv) Liquefaction of gases involves decrease in intermolecular spaces.
(v) An ideal gas on expansion will show Joule-Thomson effect.

Answers:
(i) False (ii) False (iii) True (iv) True (v) False

Q.4. *(a) What is Boyle's law of gases? Give its experimental verification.*

Solved on Page 99

(b) What are isotherms? What happens to the positions of isotherms when they are plotted at high temperature for a particular gas?

Solved on Page 100

(c) Why do we get a straight line when pressures exerted on a gas are plotted against inverse of volumes? This straight line changes its position in the graph by varying the temperature. Justify it.

Solved on Page 101

(d) How will you explain that the value of the constant K in (PV=K) in Boyle's law depend upon

(i) Temperature of the gas

According to Boyle's law PV=K at constant temperature. When temperature is increased, volume of a given mass of gas is increased. Therefore, the product PV hence k will also increase.

(ii) Quantity of the gas

According to Boyle's law PV=K at constant temperature. When quantity of gas is increased, volume of gas is increased at consant temperature. Therefore, the product PV and hence K will also increase.

Q5 (a) What is the Charles's law? Which scale of temperature is used to verify that V/T = k (pressure and number of moles are constant)?

Solved on Page 100

(b) A sample of carbon monoxide gas occupies 150 mL at 25°C. It is then cooled at constant pressure until it occupies 100 mL. What is the new temperature?

Solution:

$V_1 = 150$ mL $\qquad V_2 = 100$ mL

$T_1 = 25°C + 273 = 298$ K $\qquad T_2 = ?$

According to Charles's law

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \quad \text{or} \quad T_2 = V_2 \times \frac{T_1}{V_1} = 100 \times \frac{298}{150} = \boxed{198.7\ K}$$

(c) Do you think that the volume of any quantity of a gas become zero at -273°C. Is it not against the law of conservation of mass? How do you deduce the idea of absolute zero from this information?

No volume of a gas cannot be zero at − 273°C, since mass of gas will be destroyed. It is against the law of conservation of mass which states

Mass can neither be created nor destroyed

Since temperature − 273°C is unattainable and it is the lowest temperature. Therefore, it is taken as Absolute zero of Kelvin scale. Thus, absolute zero is defined as

The hypothetical temperature at which the volumes of all gases become zero is called absolute zero.

Q.6. (a) What is Kelvin scale of temperature? Plot a graph for one mole of an a real gas to prove that a gas becomes liquid, earlier than -273.16°C.

Solved on Page 104

(b) Throw some light on the factor 1/273 in Charles's law

According to quantitative statement of Charles's law,

At constant pressure, the volume of a given mass of an ideal gas increases or decreases by 1/273 of its original volume at 0°C for every 1°C rise or fall in temperature respectively.

- Thus, if we have 273 dm^3 of a gas at 0°C, then its $\frac{1}{273}$ part will be $\frac{1}{273} \times 273\ dm^3 = 1\ dm^3$

So, for every 1°C rise or fall in temperature, volume will increase or decrease by 1 dm^3.

- Also, if we have 546 dm^3 of a gas at 0°C, then its $\frac{1}{273}$ part will be $\frac{1}{273} \times 546\ dm^3 = 2\ dm^3$

So, for every 1°C rise or fall in temperature, volume will increase or decrease by 2 dm^3.

In both cases if temperature is decreased to − 273°C, the volume of the gas will become zero. Thus, − 273°C is taken as zero of Kelvin scale and is called Absolute zero. Hence, this factor 1/273 has helped in the development of Kelvin Scale.

Q.7. (a) What is the general gas equation? Derive it in various forms?

Solved on Page 106

(b) Can we determine the molecular mass of an unknown gas if we know the pressure, temperature and volume along with the mass of the gas.

Solved on Page 107

(c) How do you justify from general gas equation that increase in temperature or decrease of pressure decreases the density of the gas?

Solved on Page 108

(d) Why do we feel comfortable in expressing the densities of gases in the units of g/dm³ rather than g/cm³.

In gases, molecules are widely separated from each other, and small amount of gas is present in a large volume. Therefore, values of densities will be much smaller, if expressed in cm^3

Thus, a bigger unit dm^3 is used because appreciable amount of gas will be present per dm^3 of gas and values of densities will be greater. e.g. density of CH_4 at STP is 0.71 gdm^{-3} but in gcm^{-3}, it is 7.1×10^{-4} which is inconvenient.

Q.8 Derive the units for general gas constant R in general gas equation.

(a) When the pressure is in atmospheres and volume in dm^3

Since $R = \frac{PV}{nT}$

Thus $R = \frac{atm \times dm^3}{mol \times K} = atm\ dm^3\ mol^{-1}K^{-1}$

(b) When the pressure is in N/m^2 and volume in m^3.

Since $R = \frac{PV}{nT}$

Thus $R = \frac{Nm^{-2} \times m^3}{mol \times K} = Nm\ mol^{-1}K^{-1} = J\ mol^{-1}K^{-1}$

(c) When energy is expressed in ergs

In SI system, The units of R in terms of energy are $R = J\ mol^{-1}K^{-1}$

In CGS system the energy is expressed in units of erg and

$1J = 10^{7}$ erg

Therefore, units of R will be $R = erg\ mol^{-1}K^{-1}$

However, numerical value of R will be different than SI units.

Q.9 (a) What is Avogadro's law of gases?

Solved on Page 111

(b) Do you think that 1 mole of H_2 and 1 mole of NH_3 at 0°C and 1 atm pressure will have Avogadro's number of particles. If not, why?

1 mole of every substance has Avogadro's number of particles.

Thus, 1 mole of each of H_2 and N_2 will also have Avogadro's number of particles i.e. 6.02×10^{23} particles.

(c) Justify that 1 cm^3 of H_2 and 1 cm^3 of CH_4 at STP will have same number of molecules, when one molecule of CH_4 is 8 times heavier than that of hydrogen. [illegible] Exam 2001)

In gases distance between two molecules is approximately 300 times the molecular size. Thus volume occupied by gas molecules does not depend upon the molecular size of molecules. The volume of gas only depends upon the number of molecules. Hence according to Avogadro's law equal volume of H_2 and CH_4 at STP will have same number of molecules, although CH_4 molecule is 8 times heavier than H_2 molecule.

Q.10. (a) Dalton's law of partial pressures is only obeyed by those gases, which don't have attractive forces among themselves. Explain it.

Dalton's law is an ideal gas law which assumes that there are no attractive forces among the gas molecules. Hence, every gas molecule moves independently.

On mixing different gases, if they have negligible attractions for each other, then every gas molecule moves independently, exerts its full pressure and thus obeys Dalton's law.

However, if gases develop strong forces for each other on mixing, then their molecules will not be independent in their motion. Therefore, pressure exerted by each gas will be different than expected. Hence, gases with strong attractive forces do not obey Dalton's law.

(b) Derive an equation to find out the partial pressure of a gas knowing the individual moles of component gases and the total pressure of the mixture.

Solved on Page 114

(c) Explain that the process of respiration obeys the Dalton's law partial pressure.

Solved on Page 116

(d) How do you differentiate between diffusion and effusion? Explain Graham's law of diffusion.

Solved on Page 118

Q.11. (a) Gases show non-ideal behaviour at low temperature and high pressure. Explain this with the help of a graph.

Solved on Page 130

(b) Do you think that some of the postulates of kinetic molecular theory of gases are faulty? Point out these postulates.

Solved on Page 131

(c) Hydrogen and helium are ideal at room temperature, but SO_2 and Cl_2 are non-ideal. How do you explain it? (Rawalpindi Board, 2007, 2010: Lahore Board, 2012)

H_2 and He have very low liquefaction temperatures. ($H_2 = -252.87°C$ He $= -268.934°C$)

While SO_2 and Cl_2 have sufficiently high liquefaction temperatures, which are close to room temperature. ($SO_2 = -10.2°C$ $Cl_2 = -34.6°C$)

Due to very low liquefaction temperature of H_2 and He, their molecules have negligible attractions for each other at room temperature. Hence, these gases behave ideally at room temperature.

While liquefaction temperature of SO_2 and Cl_2 are close to room temperature, therefore, at room temperature, their molecules have appreciable forces of attraction. Hence SO_2 and Cl_2 are non-ideal at room temperature.

Q.14 (a) Derive van der Waal's equation for real gases.

Solved on Page 132

(b) What is the physical significance of Vander Wall's constants a and b give their units. (Multan Board, 2013)

'a'

In van der Waals equation 'a' is called as the co-efficient of attraction or attraction per unit volume. It indicates the strength of intermolecular forces in gases. Stronger the intermolecular forces, higher the value of 'a' and vice versa. Its units are Nm^4mol^{-2}

'b'

In Van der Waal's eq, 'b' is called as the effective volume (excluded volume) occupied by gas molecules in highly compressed sate but not in liquid state. It depends upon the size of gas molecules. Greater the size of gas molecules greater will be the value of 'b' and vice versa. Its units are $dm^3 mol^{-1}$

Q.15: Explain the following facts

(i) The plot of PV versus P is a straight line at constant temperature and with a fixed number of moles of an ideal gas. (D.G. Khan Board, 2012: Azad Kashmir Board, 2012)

According to Boyle's Law

At constant T, the product of pressure and volume of a fixed mass of gas is always constant. i.e. PV = K

Hence, if a graph is plotted between P on X – axis and PV on Y–axis, then a straight line parallel to X – axis is obtained, showing that PV (or K) is a constant quantity.

(ii) The straight line in (a) is parallel to x-axis and goes away from the pressure axis at higher pressure.

For real gases, when pressure is increased, the value of PV does not remain constant. At higher pressure, molecules of gases come closer together, develop forces of attraction, and thus show deviation from ideal behaviour. Hence, at high P, the straight line changes to curves and goes away from the pressure axis. The nature of curve depends upon the nature of real gas.

(iii) The van der Waals constant 'b' of a gas is four times the molar volume of gas.

The gas molecules are incompressible spheres. Thus when gas molecules are packed together like spheres, there remains some empty spaces in between the spheres which are also incompressible.

Hence, the incompressible volume 'b' is actually more than the actual molar volume of gas molecules. Actually, it is four times than their molar volume.

i.e. $b = 4V_m$

(iv) Pressure of NH_3 gas at given condition (say 20 atm pressure and room temperature) is less as calculated by Van der Waal's equation than that calculated by general gas equation. (Lahore Board, 2012)

NH_3 is a polar gas. Its molecules have forces of attraction. Thus, it shows non-ideal behaviour. Therefore, molecules of NH_3 are attracted inward while striking the wall of container. Thus, these exert less pressure than expected ideal pressure.

Hence, real pressure of NH_3 as calculated by Van der Waal's equation is less than the ideal pressure.

(v) Water vapours do not behave ideally at 273 K. (D.G. Khan Board, 2007: Lahore Board, 2012: Gujranwala Board, 2013, 2014)

273 K is the freezing point of water. At this temperature, vapours of water have appreciable forces of attraction between them. Hence water vapours behave non-ideally at 273 K

(vi) SO_2 is non-ideal at 273 K but behaves ideally at 327°C. (Multan Board, 2008: Lahore Board, 2011, 2013)

At low temperature of 273 K, molecules SO_2 gas (– 10.2°C) have considerable attractions for each other and thus SO_2 gas behaves non-ideally.

When temperature is increased to 327 K, the forces of attractions among SO_2 molecules decreases and hence SO_2 gas shows ideal behaviour at 327°C.

IMPORTANT FORMULAS

GAS LAWS

Boyle's Law

$PV = k \qquad P_1V_1 = P_2V_2$

Charles's Law

$\dfrac{V}{T} = k \qquad \dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$

General Gas Equation

$PV = nRT \qquad \dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

$M = \dfrac{mRT}{PV} \qquad d = \dfrac{PM}{RT}$

van der Waal's Equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

Avogadro's Law

To find the number of particles (atoms, ions, molecules or formula units)

$$\text{number of particles} = \frac{\text{Given Mass}}{\text{Molar Mass}} \times N_A$$

or $\quad \text{number of particles} = \text{moles} \times N_A$

Molar Mass may be Molecular mass or atomic mass or formula mass or ionic mass

Dalton's Law of Partial Pressure

$P_t = P_1 + P_2 + \ldots$

$P_tV = n_tRT \quad$ or $\quad P_gV = n_gRT$

$P_g = \dfrac{n_g}{n_t} \times P_t \quad$ or $\quad P_g = x_g \times P_t$

P_t = Total Pressure of mixture of gases $\quad P_g$ = Partial Pressure of gas in mixture

n_g = number of moles of a gas in mixture $\quad x_g$ = Mole Fraction of gas in mixture

n_t = Total number of moles of a mixture of gases

Graham's Law of Diffusion or Effusion Of Gases

$\dfrac{r_1}{r_2} = \sqrt{\dfrac{d_2}{d_1}} \qquad \dfrac{r_1}{r_2} = \sqrt{\dfrac{M_2}{M_1}}$

Kinetic Equation for an Ideal Gas

$$PV = \frac{1}{3}mN\bar{c}^2$$

NUMERICAL PROBLEMS (Exercise)

Q.16. Helium gas in a 100 cm³ container at a pressure of 500 torr is transferred to a container with a volume of 250 cm³. What will be the new pressure (a) if no change in temperature occurs (b) is temperature changes from 20°C to 15°C.

Solution:

(a) When the T is not changed

$V_1 = 100\ cm^3 \qquad V_2 = 250\ cm^3$

$P_1 = 500\ torr \qquad P_2 = ?$

According to Boyle's law

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2}$$

$$P_2 = \frac{500 \times 100}{250} = \boxed{200\ torr}$$

(b) When the T is changed

$V_1 = 100\ cm^3 \qquad V_2 = 250\ cm^3$

$P_1 = 500\ torr \qquad P_2 = ?$

$T_1 = 20°C + 273 = 293\ K \qquad T_2 = 15°C + 273 = 288\ K$

According to general gas equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P_2 = \frac{P_1V_1}{T_1} \times \frac{T_2}{V_1}$$

$$P_2 = \frac{500 \times 100}{293} \times \frac{288}{250} = \boxed{196.6\ torr}$$

Q.17. What are the densities in kg/m³ for following gases at STP (P=101325 Nm⁻², T = 273 K, Molecular mass are in kg mol⁻¹).

(i) Methane
(ii) Oxygen
(iii) Hydrogen

Solution:

(i) Methane

$T = 273\ K$

$P = 101325\ N\ m^{-2}$

Molar mass $= M = 16\ g\ mol^{-1}$

$= \frac{16}{1000}\ kg\ mol^{-1} = 0.016\ kg\ mol^{-1}$

$R = 8.314\ J\ mol^{-1}K^{-1}$

$d = ?$

The density of gas is given by

$$d = \frac{PM}{RT} = \frac{101325 \times 0.016}{8.314 \times 273}$$

$$= \boxed{0.714\ kg\ m^{-3}}$$

(ii) Oxygen

$T = 273\ K$

$P = 101325\ N\ m^{-2}$

Molar mass $= M = 32\ g\ mol^{-1}$

$= \frac{32}{1000}\ kg\ mol^{-1} = 0.032\ kg\ mol^{-1}$

$R = 8.314\ J\ mol^{-1}K^{-1}$

$d = ?$

The density of gas is given by

$$d = \frac{PM}{RT} = \frac{101325 \times 0.032}{8.314 \times 273}$$

$$= \boxed{1.428\ kg\ m^{-3}}$$

(iii) Hydrogen

$T = 273\ K$

$P = 101325\ N\ m^{-2}$

Molar mass $= M = 2\ g\ mol^{-1}$

$= \frac{2}{1000}\ kg\ mol^{-1} = 0.002\ kg\ mol^{-1}$

$R = 8.314\ J\ mol^{-1}K^{-1}$

$d = ?$

The density of gas is given by

$$d = \frac{PM}{RT} = \frac{101325 \times 0.002}{8.314 \times 273}$$

$$= \boxed{0.0893\ kg\ m^{-3}}$$

(b) Compare the values of densities in proportion to their molar masses.

Density of a gas is directly proportional to its molar masses.
Since molar masses of O_2, CH_4 and H_2 are in the order

$$O_2 > CH_4 > H_2$$

Hence, under given conditions, their densities are also in the same order.

(c) How do you justify that increase of volume upto 100 dm³ at 27°C of 2 moles of NH_3 will allow the gas behave ideally?

By increasing the volume of NH_3, the molecules of NH_3 become widely separated. As a result, forces of attraction between NH_3 molecules become less and hence it behaves ideally.

Q.18. A sample of Krypton with a volume of 6.25 dm³ and a pressure of 765 torr and a temperature of 20°C is expanded to a volume of 9.55 dm³ and a pressure of 375 torr. What will be its final temperature (in °C)

Solution:

$V_1 = 6.25\ dm^3$ $\quad V_2 = 9.55\ dm^3$

$P_1 = 765$ torr $\quad P_2 = 375$ torr

$T_1 = 20°C + 273 = 293K \quad T_2 = ?$

According to General Gas Equation

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$T_2 = \frac{T_1}{P_1V_1} \times P_2V_2$$

$$T_2 = \frac{293}{765 \times 6.25} \times 375 \times 9.55$$

$$T_2 = 219.46 \text{ K}$$

Hence T in °C = K – 273 = 219.46 – 273.16 = $\boxed{-53.7\ °C}$

Q.19. *Working at vacuum line a chemist isolated a gas in weighing bulb with a volume of 255 cm³ at a T of 25°C and under a pressure in the bulb of 10 torr. The gas weighed 12.1 mg. What is the molecular mass of this gas?*

Solution:

$$V = 255 \text{ cm}^3 = \frac{255}{1000} \text{ dm}^3 = 0.255 \text{ dm}^3$$

$$T = 25°C + 273 = 298K$$

$$P = 10 \text{ torr} = \frac{10}{760} \text{ atm} = 0.01316 \text{ atm.}$$

Mass of the gas = $m = 12.1 \text{ mg} = \frac{12.1}{1000} \text{ g} = 0.0121 \text{ g}$

$R = 0.0821$ atm. dm³ mol⁻¹ K⁻¹

Mol. Mass of gas = M = ?

According to general gas equation

$$M = \frac{mRT}{PV}$$

$$M = \frac{0.0121 \times 0.0821 \times 298}{0.01316 \times 0.255}$$

$$M = \boxed{88.23\ g/mol}$$

Q.20. *What pressure is exerted by a mixture of 2 g of H_2 and 8 g of N_2 at 273 K in a 10 dm³ vessel?*

Solution:

Mass of H_2 = 2 g

Moles of $H_2 = n_{H2} = \frac{2}{2} = 1$ moles

Mass of N_2 = 8 g

Moles of $N_2 = n_{N2} = \frac{8}{28} = 0.286$ moles

Total number of moles = $n_t = n_{H2} + n_{N2}$
$= 1 + 0.286 = 1.286$ moles

Volume of mixture = V = 10 dm³

T = 273K

R = 0.0821 atm dm³ mol⁻¹ K⁻¹

Total pressure = P_t = ?

According to General Gas Equation

$$P_tV = n_tRT$$

$$P_t = \frac{n_tRT}{V}$$

$$P_t = \frac{1.286 \times 0.0821 \times 273}{10}$$

$$= \boxed{2.88\ atm}$$

Q.21. *(a) The relative densities of two gases A and B are 1 : 1.5. Find out the volume of B, which will diffuse in the same time in which 150 dm³ of A will diffuse?*

Solution:

Since relative densities of gases A and B are 1 : 1.5

Hence relative density of gas A = d_A = 1

And relative density of gas B = d_B = 1.5

Volume of gas A diffused = 150 dm³

Volume of gas B diffused = ?

According to Graham's Law of diffusion of gases

$$\frac{r_B}{r_A} = \sqrt{\frac{d_A}{d_B}}$$

Since rate of diffusions are directly proportional to the volume of gases diffused, hence

$$\frac{\text{volume of gas B diffused}}{\text{volume of gas A diffused}} = \sqrt{\frac{d_A}{d_B}}$$

or $$\frac{\text{volume of gas B diffused}}{150} = \sqrt{\frac{1}{1.5}}$$

$$\text{volume of gas B diffused} = \sqrt{\frac{1}{1.5}} \times 150 = \boxed{122.47\ dm^3}$$

(b) Hydrogen diffuses through a porous plate at a rate of 500 cm^3 per minute at 0°C. What is the rate of diffusion of oxygen through the same porous plate at 0°C

Solution:

Rate of diffusion of hydrogen $= r_{H_2} = 500\ cm^3/min$

Rate of diffusion of oxygen $= r_{O_2} = ?$

Molecular Mass of H_2 $= M_{H_2} = 2\ g\ mol^{-1}$

Molecular Mass of O_2 $= M_{O_2} = 32\ g\ mol^{-1}$

According to Graham's Law of diffusion of gases

$$\frac{r_{O_2}}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}}$$

or $$\frac{r_{O_2}}{500} = \sqrt{\frac{2}{32}}$$

$$r_{O_2} = \sqrt{\frac{2}{32}} \times 500 = \boxed{125\ cm^3/min}$$

(c) The rate of effusion of an unknown gas A through a pinhole is found to be 0.279 times the rate of effusion of H_2 through the same pinhole. Calculate the molecular mass of the unknown gas at STP.

Solution:

Let Rate of effusion of unknown gas A $= r_A = 0.279$

Then Rate of effusion of unknown gas $= r_{H_2} = 1$

Molecular mass of hydrogen $= M_{H_2} = 2\ g/mol$

Molecular mass of unknown gas A $= M_A = ?$

According to Graham's law of effusion

$$\frac{r_{H_2}}{r_A} = \sqrt{\frac{M_A}{M_{H_2}}}$$

or $$\frac{M_A}{M_{H_2}} = \left(\frac{r_{H_2}}{r_A}\right)^2$$

or $$\frac{M_A}{M_{H_2}} = \left(\frac{r_{H_2}}{r_A}\right)^2$$

$$M_A = \left(\frac{1}{0.279}\right)^2 \times 2$$

$$M_A = 12.85 \times 2$$

$$= \boxed{25.7\ g\ mol^{-1}}$$

Q.22. *Calculate the number of molecules and the number of atoms in given amounts of each gas*

(a) 20 cm^3 of CH_4 at 0°C and a pressure of 700 mm of Hg *(Gujranwala Board, 2009)*

Solution:

$V = 20\ cm^3 = \frac{20}{1000}\ dm^3 = 0.02\ dm^3$

$T = 0°C + 273 = 273\ K$

$P = 700\ \text{mm of Hg} = \frac{700}{760}\ atm = 0.921\ atm$

$R = 0.0821\ atm\ dm^3\ mol^{-1}\ K^{-1}$

$n = ?$

According to general gas equation

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n = \frac{0.921 \times 0.02}{0.0821 \times 273} = 0.000822 \text{ mol}$$

1 mole of CH_4 contains molecules $= 6.02 \times 10^{23}$

0.000822 moles of CH_4 contains $= 6.02 \times 10^{23} \times 0.000822$

$= 4.95 \times 10^{20}$ molecules

1 molecule of CH_4 contains atoms $= 5$

4.95×10^{20} molecules contains $= 5 \times 4.95 \times 10^{20}$

$= \boxed{2.475 \times 10^{21} \text{ atoms}}$

(b) 1 ml of NH_3 at 100°C and a pressure of 1.5 atm

$V = 1 \text{ cm}^3 = \frac{1}{1000} \text{ dm}^3 = 0.001 \text{ dm}^3$

$T = 100°C + 273 = 373 \text{ K}$

$P = 1.5$ atm

$R = 0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}$

$n = ?$

According to general gas equation

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

$$n = \frac{1.5 \times 0.001}{0.0821 \times 373} = 4.9 \times 10^{-5} \text{ mol}$$

1 mole of NH_3 contains molecules $= 6.02 \times 10^{23}$

0.000049 moles of NH_3 contains $= 6.02 \times 10^{23} \times 0.000049$

$= 2.95 \times 10^{19}$ molecules

1 molecule of NH_3 contains atoms $= 4$

2.95×10^{19} molecules contains $= 4 \times 2.95 \times 10^{19}$

$= \boxed{1.18 \times 10^{20} \text{ atoms}}$

Q.23. Calculate the masses of 10^{20} molecules of each of H_2, O_2 and CO_2 at STP. What will happen to the masses of these gases, when the T of these gases is increased by 100°C and the pressure is decreased by 100 mm of Hg?

Solution:

For H_2

Number of molecules $= 10^{20}$

Mass of Hydrogen $= ?$

Since 6.02×10^{23} molecules of $H_2 = 2$ g

Therefore 10^{20} molecules of $H_2 = \frac{2}{6.02 \times 10^{23}} \times 10^{20}$

$= \boxed{3.322 \times 10^{-4} \text{ g}}$

For O_2

Number of molecules $= 10^{20}$

Mass of Oxygen $= ?$

Since 6.02×10^{23} molecules of $O_2 = 32$ g

Therefore 10^{20} molecules of $O_2 = \frac{32}{6.02 \times 10^{23}} \times 10^{20}$

$= \boxed{5.3152 \times 10^{-3} \text{ g}}$

For CO_2

Number of molecules $= 10^{20}$

Mass of Carbon dioxide $= ?$

Since 6.02×10^{23} molecules of $CO_2 = 44$ g

Therefore 10^{20} molecules of $CO_2 = \frac{44}{6.02 \times 10^{23}} \times 10^{20}$

$= \boxed{7.3084 \times 10^{-3} \text{ g}}$

The change in T and P has no effect on masses of gas.

Q.24. Two moles of NH_3 are enclosed in a 5 dm³ flask at 27°C.
(a) Calculate the pressure exerted by the gas assuming that
i. Gas behaves like an ideal gas
ii. Gas behaves like a real gas
$a = 4.17 \text{ atm dm}^6 \text{ mol}^{-2}$ $b = 0.0371 \text{ dm}^3 \text{ mol}^{-1}$

Solution:

(i) When the gas is ideal

$V = 5 \text{ dm}^3$

$n = 2$ mol

$T = 27°C + 273 = 300 \text{ K}$

$R = 0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{K}^{-1}$

$P = ?$

According to general gas equation

$$PV = nRT$$

Or $P = \frac{nRT}{V}$

$$P = \frac{2 \times 0.0821 \times 300}{5}$$

$$P = \boxed{9.852 \text{ atm}}$$

(ii) When the gas is real

$V = 5\ dm^3$

$n = 2\ mol$

$T = 27°C + 273 = 300\ K$

$R = 0.0821\ atm\ dm^3\ mol^{-1}K^{-1}$

$a = 4.17\ atm\ dm^6\ mol^{-2}$ $b = 0.0371\ dm^3\ mol^{-1}$

$P = ?$

According to Van der Waal's eq

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

or $$\left(P + \frac{an^2}{V^2}\right) = \frac{nRT}{(V - nb)}$$

or $$P = \frac{nRT}{(V - nb)} - \frac{an^2}{V^2}$$

Putting values

$$P = \frac{2 \times 0.0821 \times 300}{(5 - 2 \times 0.0371)} - \frac{4.17 \times 2^2}{5^2}$$

$$P = \frac{49.26}{4.926} - \frac{16.68}{25}$$

$$P = 10 - 0.67$$

$$P = \boxed{9.33 \text{ atm}}$$

(b) Also calculate the amount of pressure lessened due to forces of attractions at these conditions of volume and temperature.

Amount of pressure lessened = 9.85 − 9.33 = 0.52 atm

(c) Do you expect the same decreases of pressure when 2 moles of NH_3 is maintained in a volume of 40 dm^3 and T of 27°C

If the volume of the gas is increased to 40 dm^3, then the pressure of gas will be less as compared to that calculated above in part (a).

It is because since volume is large, therefore molecules will be more widely spaced than before and they will have lesser forces of attractions. Hence gas will be more ideal and pressure difference form ideal behaviour will also be small.

HELLO! Mr. Question here!

Multiple Choice Questions from PAST PAPERS

1. If "a" and "b" are zero for certain gas then gas is: *(Lahore board, 2014)*
   (a) Ideal (b) Real (c) Non - ideal (d) May be any diatomic gas
2. Escape out of gas molecules one by one through tiny hole is: *(Lahore board, 2014)*
   (a) Diffusion (b) Effusion (c) Osmosis (d) All of these
3. The spreading of fragrance or scent in air is due to: *(Rawalpindi board, 2011)*
   (a) Effusion (b) Diffusion (c) Osmosis (d) Density
4. Partial pressure of O_2 in lungs (in torr) is: *(Gujranwala board, 2008)*
   (a) 150 (b) 760 (c) 116 (d) 159
5. The constant factor in Charle's law is: *(Gujranwala board, 2008)*
   (a) volume (b) temperature (c) pressure (d) all of these
6. Partial pressure of oxygen in human lungs in torr is: *(Gujranwala board, 2011)*
   (a) 161 (b) 116 (c) 159 (d) 760
7. The S.I. unit of pressure is expressed in (Rawalpindi Board, 2013) (Multan Board, 2013)
   (a) Nm^{-1} (b) Nm^{-2} (c) Nm^{-3} (d) mm Hg
8. Which gas will diffuse more rapidly: *(Lahore Board, 2009)*
   (a) CO_2 (b) NH_3 (c) HCl (d) SO_2
9. Plasma is conductor of electricity: *(Faisalabad Board, 2009)*
   (a) Bad (b) Poor (c) Good (d) None
10. SI unit of pressure is: *(Rawalpindi Board, 2009)*
    (a) torr (b) mmHg (c) Nm^{-2} (d) pound $inch^{-2}$
11. Density of an ideal gas can be calculated by the formula. *(Faisalabad Board, 2011)*
    (a) $d = nRT$ (b) $d = \frac{PM}{RT}$ (c) $d = \frac{m}{M}RT$ (d) $d = \frac{PV}{M}$
12. Absolute zero is equal to *(Lahore Board, 2007)*
    (a) 273°C (b) -273°C (c) 0°C (d) 273K
13. Which gas will diffuse more rapidly among the following? *(D.G. Khan Board, 2010)*
    (a) N_2 (b) H_2 (c) CO (d) NH_3
14. To calculate the pressure of volume of a real gas under the non-ideal conditions, alternative kinetic equation has been developed. This is known as: *(Faisalabad Board, 2010)*
    (a) General gas equation (b) Arrhenius equation
    (c) Clasius Clapeyron equation (d) Vander Wall's equation

15. An ideal gas has volume 1 dm^3 at 303 K. Keeping pressure constant, at which Kelvin temperature its volume becomes 2 dm^3 (Sargodha Board, 2011)
(a) 240 (b) 303 (c) 330 (d) 606

16. Which gas will diffuse more rapidly (Sargodha Board, 2014)
(a) CO_2 (b) NH_3 (c) HCl (d) SO_2

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(a)	2	(b)	3	(b)	4	(c)	5	(c)
6	(b)	7	(b)	8	(b)	9	(c)	10	(c)
11	(b)	12	(b)	13	(b)	14	(d)	15	(d)
16	(b)								

Detailed Explanation of Past Papers MCQs & answers to all Past Papers SHORT QUESTONS in COLLEGE CHEMISTRY OBJECTIVE BOOK-I

SHORT & LONG QUESTIONS FROM PAST PAPERS

PRESSURE, BOYLE'S LAW, CHARLES'S LAW

Short Questions

(1) Define pressure. Give its units. (Lahore Board, 2009: Multan Board, 2009: D.G. Khan Board, 2011: Sargodha Board, 2012) OR Compare the different units of pressure. (Sargodha Board, 2007)
(2) Define Boyle's law. Give its expression. (Faisalabad Board, 2009, 2012: Gujranwala Board, 2013)
(3) The product of pressure and volume at constant temperature and number of moles is constant. Why? (Sargodha Board, 2009)
(4) Why the graph plotted between pressure and volume moves away from pressure axis at higher temperature. (Sargodha Board, 2013)
(5) Why do we get a straight line when pressure are plotted against inverse volume of a gas. (Bahawalpur Board, 2009: Gujranwala Board, 2011: Rawalpindi Board, 2013)
(6) Greater the temperature of the gas, closer the straight line of P versus 1/V to the pressure axis. Justify it. (Lahore Board, 2007)
(7) State Charle's Law and write its mathematical form (Multan Board, 2012)
(8) Volume of a gas is doubled when temperature is raised from 0°C to 273°C. Why? (Bahawalpur Board, 2008)

Long Questions

Define Boyle's law. Give its experimental verification. (Bahawalpur Board, 2011)

ABSOLUTE ZERO

Short Questions

(1) Give the quantitative definition of Charles's law? (Faisalabad Board, 2008: Bahawalpur Board, 2012)
(2) What do you mean by absolute zero? (Faisalabad Board, 2008: Bahawalpur Board, 2008: Sargodha Board, 2009: D.G. Khan Board, 2012) **OR** What is absolute zero? What happens to real gases while approaching it? (Sargodha Board, 2012: Faisalabad Board, 2013)
(3) The volume of a given mass of a gas becomes theoretically zero at -273°C. Justify it. (Rawalpindi Board, 2007, 2009: Lahore Board, 2014)

SCALES OF THERMOMETRY

Short Questions

(1) What are different scales of thermometry? OR What is thermometry? Name the scales and device used for thermometry. (Multan Board, 2011) OR How the various scales of thermometry can be interconverted? (Lahore Board, 2007)
(2) Give two important scales of thermometry. How are these related? (Lahore Board, 2008: Faisalabad Board, 2009)
(3) -273°C is regarded as the lowest possible temperature. Justify it. (Gujranwala Board, 2010)
(4) Volume of real gas cannot be zero at any temperature. Why? (Sargodha Board, 2007)
(5) Convert 80°C to Fahrenheit scale. (Faisalabad Board, 2010)
(6) Convert 40°F to Kelvin temperature (Bahawalpur Board, 2010)
(7) Convert – 40°F to (a) Centigrade scale (b) Kelvin scale (D.G. Khan Board, 2011)
(8) Convert -40°C to °F (Faisalabad Board, 2012)
(9) Convert -40°F temperature to kelvin temperature. (Rawalpindi Board, 2012)

GENERAL GAS EQUATION, IDEAL GAS CONSTANT

Short Questions

(1) What is general gas equation? Derive it in various forms. (Multan Board, 2010)
(2) Derive the unit of 'R' in general gas equation when the pressure is in atmosphere and volume in dm^3 (Multan Board, 2012)
(3) Calculate the value of R in SI units OR Derive the units for gas constant R in general gas equation when pressure is in Nm^{-2} and volume in m^3 (Lahore Board, 2008, 2013: Gujranwala Board, 2011, 2013, 2014: Multan Board, 2008, 2012: D.G. Khan Board, 2009: Rawalpindi Board, 2009, 2010: Sargodha Board, 2012, 2013)
(4) Derive general gas equation for one mole of a gas? (Gujranwala Board, 2011)

AVOGADRO'S LAW, DALTON'S LAW OF PARTIAL PRESSURE AND ITS APPLICATIONS.

Short Questions

(1) What is Avogadro's law of gases? (Rawalpindi Board, 2010: (Sargodha Board, 2014: Lahore Board, 2014) **OR** Explain Avogadro's law with example (D.G. Khan Board, 2012)
(2) Define Dalton's law of partial pressure. Give an example. (Lahore Board, 2009: Gujranwala Board, 2011: Bahawalpur Board, 2011) **OR** Define Dalton's law of partial pressure. Give mathematical expression (Faisalabad Board, 2011: Azad Kashmir Board, 2012)
(3) Prove that $P_i = P_t X_i$ (Lahore Board, 2014)

(4) The process of respiration obeys the Dalton's law of partial pressure. Justify. **(D.G. Khan Board, 2012: Sargodha Board, 2013)**
(5) Why pilots (or we) feel uncomfortable breathing at high altitude? **(Faisalabad Board, 2007, Sargodha Board, 2010, 2011)**
(6) Why regular air cannot be used in divers tank? **(Lahore Board, 2010)** **OR** Explain procedure of sea divers breath. **(Rawalpindi Board, 2011)**
(7) How Dalton's law of partial pressure is useful in determining pressure of a gas collected at water? **(D.G. Khan Board, 2010: Multan Board, 2011)**
(8) Explain two applications of Dalton's law of partial pressures. **(D.G. Khan Board, 2007; Gujranwala Board, 2012) Ans: Combine S1 and S4**
(9) Calculate fraction of total pressure exerted by oxygen when equal masses of CH_4 and O_2 are mixed in an empty container at 25°C. **(Lahore Board, 2014)**

Long Questions

(1) Describe Dalton's law of partial pressure. Write its two/three/four applications. **(Lahore Board, 2010: Faisalabad Board, 2011: Lahore Board, 2013: Gujranwala Board, 2013)**
(2) What are the applications of Dalton's law of partial pressure? **(Sargodha Board, 2014) OR** Write down the applications of Dalton's Law of Partial Pressure. **(Rawalpindi Board, 2010)**

DIFFUSION, EFFUSION, GRAHAM'S LAW OF DIFFUSION

Short Questions

(1) Define diffusion and effusion. **(Faisalabad Board, 2013: Sargodha Board, 2013)**
(2) Differentiate between diffusion and effusion of gases. **(Faisalabad Board, 2007: Bahawalpur Board, 2012)**
(3) State Graham's law of diffusion and write its mathematical form. **(D.G. Khan Board, 2011: Rawalpindi Board, 2012)**
(4) Rate of diffusion of NH_3 gas is more than HCl gas. Why? **(Bahawalpur Board, 2011) OR** Lighter gases can diffuse more rapidly than heavier gases. Why? **(Gujranwala Board, 2008, 2009: D.G. Khan Board, 2009)**

Long Questions

(1) Define and verify Graham's law of diffusion of gases. **(Faisalabad Board, 2010: D.G. Khan Board, 2011)**
(2) State and explain Graham's Law of diffusion of gases. **(Lahore Board, 2011)**

KINETIC MOLECULAR THEORY OF GASES

Short Questions

(1) List four postulates of kinetic molecular theory of gases. **(Faisalabad Board, 2011: Lahore Board, 2015)**
(2) Give mathematic expression of Kinetic equation and root mean square velocity. **(Multan Board, 2012)**
(3) Give mathematical expression for mean square velocity and root mean square velocity. **(Rawalpindi Board, 2009)**
(4) Why gases do not settle down in a vessel? **(Gujranwala Board, 2008)**
(5) What are elastic collisions? Give an example. **(Multan Board, 2007)**

Long Questions

(1) What is Kinetic molecular theory of gases. Give its Postulates. **(Sargodha Board, 2013)**

EXPLANATION OF GAS LAWS ON THE BASIS OF KINETIC MOLECULAR THEORY OF GASES

Short Questions

(1) Explain Boyle's law according to kinetic molecular theory of gases. **(Lahore Board, 2013, 2014)**
(2) Apply kinetic molecular theory to explain the Avogadro's Law. **(Sargodha Board, 2011)**
(3) Derive Graham's law of diffusion from kinetic molecular theory of gases. **(Gujranwala Board, 2008)**

Long Questions

(1) Define Graham's law. Explain Graham's law of diffusion according to kinetic equation. **(D.G. Khan Board, 2010)**
(2) Explain Avogadro's law and Graham's law of diffusion on the basis of Kinetic Molecular Theory of gases. **(Multan Board, 2011)**
(3) What is kinetic molecular theory of gases? Derive Boyle's law from kinetic equation. **(Faisalabad Board, 2013)**
(4) How are Boyle's law and Charle's law derived from kinetic molecular theory of gases? **(Multan Board, 2013)**

CRITICAL TEMPERATURE, PRESSURE, LIQUEFCATION OF GASES, LINDE'S METHOD

Short Questions

(1) Define critical temperature and pressure. **(Sargodha Board, 2010) OR** Differentiate between critical temperature and critical pressure. **(Gujranwala Board, 2012)**
(2) What is the critical temperature of a gas? Give its importance for liquefaction of gases **(D.G. Khan Board, 2008: Faisalabad Board, 2009; Bahawalpur Board, 2012)**
(3) What is critical temperature? It depends upon what factors? **(D.G. Khan Board, 2010: Multan Board, 2013)**
(4) State Joule-Thomson effect. What is its applications? **(Lahore Board, 2010: Faisalabad Board, 2010: Bahawalpur Board, 2010: Gujranwala Board, 2012)**
(5) Explain Linde's method of liquefaction of gases. **(Multan Board, 2010)**
(6) Joule-Thomson effect is operative in the Linde's Method of Liquefaction of air. How? **(Lahore Board, 2007)**
(7) State Joule-Thomson effect. Why it is not applicable to H_2 gas? **(Lahore Board, 2011)** **OR** Ammonia gas can be liquefied quite easily than H_2 gas. Justify it. **(D.G. Khan Board, 2008)**

Long Questions

(1) Describe Linde's method of liquefaction of gases. **(Lahore Board, 2013)**

IDEAL AND NON-IDEAL GASES, CAUSES OF DEVIATION

Short Questions

(1) What is compressibility factor? What is its value for an ideal gas? **(Multan Board, 2007)**
(2) What are faulty points in kinetic molecular theory of gases? **(Faisalabad Board, 2008: Lahore Board, 2009: Bahawalpur Board, 2011: Lahore Board, 2012)** OR Describe two causes of deviation from ideality. **(Gujranwala Board, 2009: Rawalpindi Board, 2011, 2013)** **OR** Why real gases deviate from ideal behaviour? **(Bahawalpur Board, 2010: Faisalabad Board, 2010: D.G. Khan Board, 2012: Sargodha Board, 2011, 2012, 2014)**
(3) Why high pressure and low temperature make a gas non-ideal? **OR** Gases deviate significantly at high pressure and low temperature. **(Sargodha Board, 2007, 2010: Gujranwala Board,**
(4) **2010: Faisalabad Board, 2011, 2012: Multan Board, 2012: Multan Board, 2013)**

(5) *Gases deviate from ideal behaviour more significantly at high pressure. Why?* (Multan Board, 2007: Bahawalpur Board, 2009)

Long Questions

(1) *Why real gases deviate from the ideal behaviour? Discuss its causes.* (Sargodha Board, 2011)

VAN DER WAAL'S EQUATION

Short Questions

(1) *Why the pressure correction is done by van der Waals?* (Rawalpindi Board, 2007: Multan Board, 2009: D.G. Khan Board, 2010)

(2) *Give (S.I.) units of 'a' and 'b' in van der Waals equation.* (D.G. Khan Board, 2009, 2011: Rawalpindi Board, 2012: Multan Board, 2012: Faisalabad Board, 2013: Rawalpindi Board, 2013)

(3) *Gases deviate more from ideal behaviour at 0°C than at 100°C. Why?* (Lahore Board, 2008)

Long Questions

(1) *Derive Vander Waal's equation for real gases.* (Multan Board, 2010: Bahawalpur Board, 2010)

(2) *Derive Vander Waal's equation for real gases and give the physical significance of van der Waal's constants 'a' and 'b'.* (Sargodha Board, 2013)

PLASMA STATE

Short Questions

(1) *What is plasma state (or fourth state of matter)? How it is formed?* (D.G. Khan Board, 2008: Bahawalpur Board, 2009: Multan Board, 2011)

(2) *Where is the plasma formed (or found)?* (Bahawalpur Board, 2008: Multan Board, 2009: Gujranwala Board, 2009)

(3) *What are characteristics of plasma?* (Multan Board, 2008: Azad Kashmir Board, 2012)

(4) *What is plasma? Write four uses (or applications) of plasma.* (D.G. Khan Board, 2007: Multan Board, 2010, 2012: Bahawalpur Board, 2012: D.G. Khan Board, 2012: Rawalpindi Board, 2012: Gujranwala Board, 2012, 2014: Lahore Board, 2011, 2013: Sargodha Board, 2013)

(5) *State what is natural and artificial plasma* (Faisalabad Board, 2012)

Long Questions

(1) *What is plasma? Give three applications of plasma.* (Sargodha Board, 2010)

TEST YOUR SKILLS Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) If absolute temperature of a gas is doubled and the pressure is also doubled, the volume of the gas will
(a) remain unchanged (b) increase four times (c) reduce to ¼ (d) be doubled

(ii) Charle's law is applicable to
(a) ideal gases (b) real gases (c) all gases (d) none

(iii) Partial pressure of O_2 in lungs (in torr) is?
(a) 150 (b) 760 (c) 116 (d) 159

(iv) If 2 moles of an ideal gas at 546 K occupy a volume of 44.8 liters, the pressure must be
(a) 2 atm (b) 3 atm (c) 4 atm (d) 1 atm

(v) The rate of diffusion of H_2, compared with He is
(a) ½ times (b) 1.4 times (c) 2 times (d) 4 times

(vi) The constant factor in charle's law is:
(a) volume (b) temperature (c) pressure (d) all of these

(vii) The molar volume of helium is 44.8 dm^3 at
(a) 100°C and 1 atm (b) 25°C and 0.25 atm (c) 0°C and 0.5 atm (d) 40°C and 0.5 atm

(viii) The total pressure exerted by a number of non-reacting gases is equal to the sum of the partial pressures of the gases under the same condition is known as
(a) Boyle's law (b) Avogadro's law (c) Charle's law (d) Dalton's law

(ix) An ideal gas has volume 1dm^3 at 303K keeping pressure constant at which Kelvin temperature its volume will become 2dm^3
(a) 240 (b) 303 (c) 330 (d) 606

(x) Which of the following gases will have the highest rate of diffusion?
(a) O_2 (b) CO_2 (c) NH_3 (d) N_2

(xi) The van der Waal's equation explains the behaviour of
(a) ideal gas (b) real gases (c) liquids (d) non-real gases

(xii) Absolute zero is equal to
(a) -273.15 K (b) -273.15 °F (c) -273.15 °C (d) 0°C

(xiii) The value of R is SI units is
(a) 0.0821 dm^3. atm. J^{-1} $mole^{-1}$ (b) 62.4 dm^3 .torr K^{-1} mole
(c) 8.31 dm^3 atm. K^{-1} $mole^{-1}$ (d) 8.31 JK^{-1} $mole^{-1}$

(xiv) One dm^3 of O_2 at STP has mass
(a) 32g (b) 16g (c) 4.438g (d) 1.428g

(xv) The volume of 1 mole of N_2 is maximum at
(a) 0°C and 2 atm (b) STP (c) 100°C and 1 atm (d) 150°C and atm

(xvi) The critical temperature for NH_3 is
(a) less than Argon (b) equal to Argon (c) greater than Argon (d) Not known

(xvii) The highest temperature above which a gas cannot be liquefied is called as
(a) Critical temperature (b) Absolute (c) Liquefaction (d) Boiling point

SUBJECTIVE

Time: 2:10 Hours **Marks: 68**

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question number carefully. (22x 2)=44

Section - I

Q2. Answer any Eight parts from the followings.

(i) What is Joule-Thomson effect?
(ii) What is absolute zero?
(iii) What is the physical significance of van der Waals constants 'a' and 'b'?
(iv) What is plasma? Where it is found?

(v) Gases behave ideally at high temperature and Low pressure. Why?
(vi) How does heat transfer from a hot body to cold body?
(vii) Prove Grahams Law of diffusion of gases.
(viii) Differentiate between an ideal & a non ideal gas.
(ix) Dalton's law of partial pressure is not obeyed by polar gases. Why?
(x) 1 dm^3 of H_2 at STP weighs 0.0899g & 1 dm^3 of O_2 at STP weight 1.3438 g, but they have same volume why?
(xi) Calculate the value of R in SI units.
(xii) Why gases diffuse into each other?

Q3. Answer any Six parts from the followings.
(i) Why the graph between 1/V on x-axis and P on Y-axis is a straight line?
(ii) What is the effect of increasing temperature on isotherm of a given mass of a gas?
(iii) The graph PV on y-axis and P on x-axis is a straight line parallel to x-axis. Why?
(iv) What is the general equation?
(v) Why pilots feel uncomfortable breathing at high altitude?
(vi) How can Charles's law be obtained from the general gas equation PV = nRT?
(vii) What is the effect of temperature and pressure on the density of a gas?
(viii) Dalton's law of partial pressure is not obeyed by a mixture of NH_3 and SO_2 gases. Why?
(ix) Why gases collected over water are impure gases?
(x) How is artificial plasma produced?
(xi) Why fluorescent tube produce light?
(xii) Lighter gases diffuse more rapidly than heavier gases explain?

Q4. Give the short answers (only 06 questions).
(i) Why real gases deviate from ideal behaviour?
(ii) Why did van der walls correct the pressure in the general gas equation?
(iii) The product of pressure and volume at constant temperature and number of moles is constant why?
(iv) Why spiral pipe is used in Lind's apparatus for liquefaction of gases?
(v) Why high pressure and low temperature make gas non ideal?
(vi) In solids, liquids and gases, temperature is the measure of which kind of energies?
(vii) Define Critical temperature and critical pressure?
(viii) The volume of the given mass of a gas becomes theoretically zero at 273°C. justify it?
(ix) Polar gases have high critical temperature. Why?

Section – II (Attempt any three questions) (8x 3)=24

Q5. (a) How general gas equation can be used to determine the molecular mass of a gas. (03)
(b) Calculate the mass of 11.2 dm^3 of H_2 at 0°C and 2 atm pressure considering hydrogen to be ideal under these condition (03)
(c) Prove Avogadro's law using kinetic equation of kinetic molecular theory. (02)

Q6. (a) Derive van der Waals equation for real gases (04)
(b) Three moles of SO_2 are enclosed in a 5 dm^3 flask at 27°C. (04)
(i) Calculate the pressure exerted by the gas assuming that
(a) Gas behaves like an ideal gas
(b) Gas behaves like a real gas For SO_2 a = 6.170 atm dm^6 mol^{-2} b = 0.0564 dm^3 mol^{-1}
(ii) Also calculate the amount of pressure lessened due to forces of attractions at these conditions of volume and temperature

Q7. (a) What are ideal and non-ideal gases? Why do real gases deviate from ideal behaviour? Explain with graph. (03)
(b) What pressure is exerted by a mixture of 2 g of He, 16 g of O_2 and 10 g of CO_2 at 10°C in a 5 dm^3 vessel? (03)
(c) Write a short note on Absolute zero. (02)

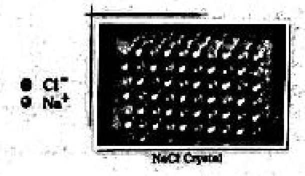
Q8. (a) What is the role of critical temperature in the liquefaction of gases? Describe Lind's method for the liquefaction of gases. (04)
(b) Write down the postulates of kinetic molecular theory of gases. (04)

Q9. (a) Give experimental verification of Graham's law. (03)
(b) Derive the expression between kinetic energy and temperature for a gas using kinetic equation for gases (03)
(c) The rate of effusion of an unknown gas A through a porous plate is found to be 1/4 times the rate of effusion of H_2 through the same porous plate. Calculate the molecular mass of the unknown gas at STP. (02)

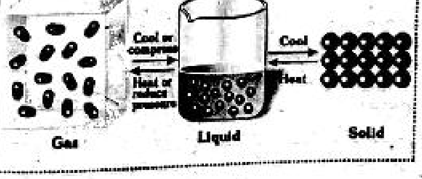
Chapter 4

LIQUIDS AND SOLIDS

van der Waal's

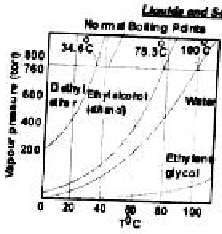


NaCl Crystal



CONTENTS

Chapter-4 **Liquids and Solids**



INTRODUCTION

Liquids have indefinite shape but definite volume.

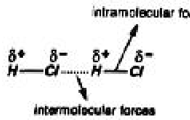
In liquids, Intermolecular distance is greater than solids but less than gases and intermolecular forces are stronger than gases but weaker than solids.

INTERMOLECULAR AND INTRAMOLECULAR FORCES

Intermolecular Forces

The forces of attraction between separate molecules of substances are called intermolecular forces

- These forces are called van der Waals forces.
- These forces are present among all types of atoms and molecules when they are close to each other.
- The physical properties of substances e.g. melting point, boiling point etc. depend upon the strength of intermolecular forces
- These forces have no relation with valence electrons.
- These forces are weaker than intramolecular forces.



Examples:

Dipole-Dipole forces; London dispersion forces etc.

Intramolecular Forces

The forces of attractions between atoms within a molecule are called intramolecular forces.

Examples:

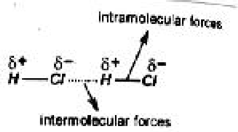
Chemical bonds i.e. ionic bond, covalent bond, co-ordinate covalent bond.

- They have almost no relation with physical properties of substances.

- These forces have concern with valence electrons.
- These forces are stronger than intermolecular forces.

- ***Intramolecular forces are stronger than intermolecular forces.***

Consider HCl. In this, a covalent bond is present between H and Cl. Both atoms complete their valence shell. Thus, they tend to always remain together. Hence, this linkage is very strong. While, in intermolecular forces only a weak electrostatic attraction is present between $Cl^{\delta-}$ of one molecule and $H^{\delta+}$ of other molecule. So, this linkage is weak.



Types of Intermolecular Forces

Intermolecular forces are also called van der Waals forces, especially when the molecules are close to each other.

There are many types of intermolecular forces

Following are the common types

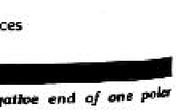
1. Dipole – dipole forces
2. Ion – dipole forces
3. Dipole – induced dipole forces
4. Instantaneous dipole – induced dipole forces or London forces

Dipole – Dipole Forces

The electrostatic forces which are developed when a negative end of one polar molecule attracts the positive end of other molecule are called dipole-dipole forces.

Example and Explanation

- Consider a bond between two different atoms e.g. H – Cl. In HCl, Cl is more electronegative than H. It attracts shared electrons more towards itself. Thus, Cl gets partial negative charge (δ^-), while H gets partial positive charge (δ^+).



- Such a bond is called polar bond and the molecule is called a dipole.
- So, when molecules are close to each other, they tend to line up and attract each other. However, thermal energy of molecules does not permit perfect alignment.
- These forces are approximately one percent as effective as a covalent bond.

Factors affecting Dipole-Dipole forces

The strength of dipole-dipole forces depends upon

- ***Difference in electronegativity of the bonded atoms***

Greater the electronegativity difference, more polar is the bond, hence, stronger the dipole-dipole forces and vice versa.

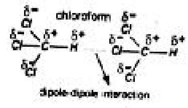
Example: Dipole-dipole forces in

- Distance between molecules.

Larger the distance between molecules, weaker the dipole dipole forces and vice versa.

Example: in gases, molecules are widely separated, therefore, these forces are very weak.

In liquids, molecules are close to each other, therefore, these forces are stronger.



Effect of Dipole-Dipole forces on Physical Properties

- The physical properties of substances e.g. melting point, boiling point etc. depend upon the strength of dipole-dipole forces.
- Generally, stronger the dipole–dipole forces greater the values of thermodynamic properties of a substance like melting points, boiling points, heat of vaporization and heat of sublimation etc.

Dipole – Induced Dipole Forces Or Debye Forces

The electrostatic forces of attraction between permanent dipole of one molecule and induced dipole of another molecule are called dipole–induced dipole forces.

Example

These are present in a mixture of polar and non – polar molecules. In this mixture, positive end of polar molecule attracts mobile electrons of non-polar molecules.

Figure: Dipole-induced dipole forces

Thus, dipole is induced in non-polar molecules. The force of attraction between polar molecule and induced dipole is called dipole–induced dipole force or Debye force.

Instantaneous Dipole–Induced Dipole Forces or London Dispersion Forces

The momentary force of attraction between instantaneous dipole and induced dipole is called instantaneous dipole – induced dipole force or London dispersion force.

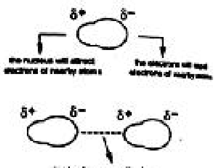
Non-polar He gas can be liquefied, which shows that its molecules have forces of attraction. To account for such things, Fritz London, a German physicist, explained these forces in 1930. These are called London dispersion forces.

Example:

These forces are more prominent in non-polar molecules e.g. H_2, N_2, noble gases etc. In polar molecules attractive forces are due to formation of the dipoles. However, in non-polar molecules, dipoles are not present under normal conditions.

Mechanism of Formation

- Consider non-polar He molecules. When two He molecules come closer to each other, their electrons repel each other and are pushed away. Therefore, a temporary dipole is produced in the molecules. Thus, electron density of molecule is no more symmetrical and it becomes a dipole. *This is called instantaneous dipole*.
- The positive end of instantaneous dipole attracts electrons of another molecule. In this way, a dipole is induced in the nearby molecule, as well. *This is called induced dipole*.



- The force of attraction is then developed between instantaneous dipole and induced dipole. It is called instantaneous dipole–induced dipole force or London dispersion force.
- These forces are developed only for few moments because electrons are moving continuously.
- The temporary dipole is finished very soon. However, a new dipole will appear in some other direction and thus weak forces are again developed between molecules.
- These forces are present in all types of molecules (polar and non-polar). However, these are more prominent in non-polar molecules e.g. H_2, Cl_2, noble gases etc.
- London forces are weaker than dipole – dipole forces

Polarizability

The measurement of the extent to which the electron cloud can be distorted or polarized is called Polarizability.

A specie (atom, ion, and molecule) is said to be polarized if temporary dipoles are created in it by the distortion of electron cloud.

Factors affecting London Forces

1. Size of Electronic Cloud

Larger the size of atoms and molecules, dispersion is easy and polarizability is high. Hence London forces are stronger.

Examples:

- ***Boiling points of Noble Gases and Halogens Increases Down The Group In Periodic Table***

Noble gases are monatomic gases. They do not form covalent bonds among themselves because their outermost shells are complete.

In Noble gases, electronic cloud size increases down the group in periodic table due to increase in atomic size. Thus, atoms are easily polarized down the group, and develop strong London forces.

That's why boiling points of noble gases increases down the group.

Similarly boiling points of halogens (VII A) also increases down the group.

- ***Halogens have different physical states at room temperature.***

Halogens are non-polar diatomic molecules.

F_2 and Cl_2 are gases, Br_2 is liquid while I_2 is solid.

It is because, electronic cloud size increases down the group in periodic table due to increase in atomic size.

Thus, atoms are easily polarized down the group, and develop strong London forces. Hence physical states of halogens changes down the group and boiling points also increases. e.g. boiling point of F_2 is −188.1°C while boiling point of iodine is +184.4°C. It is because polarizability of iodine is much greater than fluorine due to larger size.

VIIA	VIII A
	2 He -268.6
9 F -188.1	10 Ne -245.9
17 Cl -34.6	18 Ar -185.7
35 Br 58.8	36 Kr -152.3
53 I 184.4	54 Xe -107.1
	86 Rn -61.8

Atomic Number
Boiling point

2. Number of Atoms in a Molecule

Generally, greater the number of atoms, stronger the London forces and vice versa.

Greater number of atoms means greater polarizability and hence stronger London forces

- ***Ethane (C_2H_6) have lower boiling point (−88.6°C) than hexane, C_6H_{14}(68.7 °C).***

Although both C_2H_6 and C_6H_{14} are non-polar. However, due to larger number of atoms in C_6H_{14}, it has stronger forces of attraction than C_2H_6.

It is because, larger hexane molecule has more places for attraction and greater polarizability than smaller ethane molecule. So, it has stronger forces and higher boiling point. Further, due to stronger forces, hexane is a liquid while ethane is a gas at room temperature.

- ***Physical state of hydrocarbons changes with increasing molecular mass***

Physical states of hydrocarbons changes from gas to liquid to solid with increasing molecular mass. It is because larger molecules have more places for attraction and greater polarizability than smaller molecules. So, they develop stronger forces. Hence, melting and boiling points also increases with increase in molecular masses.

Table 4.2 Boiling points and physical states of some hydrocarbons

Name	B.P. °C (1 atm)	Physical state at S.T.P	Name	B.P. °C (1 atm)	Physical state at S.T.P
Methane	−161.5	Gas	Pentane	36.1	Liquid
Ethane	−88.6	Gas	Hexane	68.7	Liquid
Propane	−42.1	Gas	Decane	174.1	Liquid
Butane	−0.5	Gas	Isodecane	327	Solid

Hydrogen Bonding

The electrostatic interaction between a strong electronegative atom and partial positively charged hydrogen atom is called hydrogen bonding.

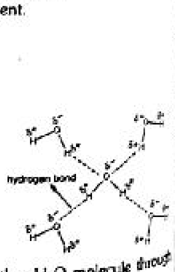
The strong electronegative elements are mostly N, O, F and rarely Cl.

Two molecules involved in H-bonding may be same or different.

Example & Explanation

Hydrogen bonding in H_2O

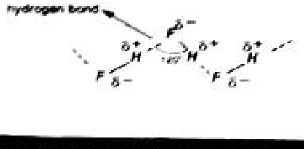
Consider H_2O. In H_2O, strong electronegative O attracts shared pair of electrons more towards itself. Thus O gets large δ^- charge and H gets large δ^+ charge. Thus, dipole-dipole interaction may be developed among water molecules. However, forces of attraction among water molecules are stronger than simple dipole-dipole interaction.

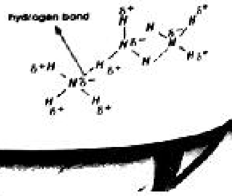


Oxygen has two lone pairs of electrons. Moreover, 'H' creates a strong electric field due to its small size. Thus, the oxygen atom of one H_2O molecule links to the H-atom of another H_2O molecule through lone pair by a co-ordinate covalent bond. This bond formed is called hydrogen bond.

Hydrogen bonding in HF and NH_3

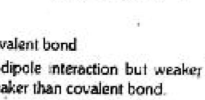
Hydrogen bond between HF and NH_3 molecules are represented as





Hydrogen bonding in acetone and chloroform

Some elements (other than N, O, and F) are also involved in H-bonding, e.g. in chloroform, the three Cl atoms makes the carbon highly δ^+ which in turn makes the H-atom also highly δ^+. This H-atom can now form H-bond with strong electronegative atom of other molecule e.g. with oxygen atom of acetone as shown in the fig.



Properties of Hydrogen Bond

- Hydrogen bond is longer than normal covalent bond
- Hydrogen bond is stronger than dipole-dipole interaction but weaker than normal covalent bond. It is generally 20 times weaker than covalent bond.
- Hydrogen bond is a directional bond
- Hydrogen bond results in the formation of long chains and network of molecules.

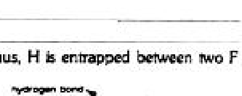
Properties and Application of Compounds Containing Hydrogen-Bonding

1. Strength of Acids

- ***HF is a Weaker Acid than HCl, HBr and HI***

In HF, molecules are H-bonded in a zigzag manner. Thus, H is entrapped between two F atoms as shown in the fig.

Thus, HF cannot easily donate its H^+ ions easily, hence it is a weaker acid.



2. Thermodynamic Properties of Covalent Hydrides

In covalent hydrides of Group IV A to VII A, H-bonding effects are very clear.

Consider the graph for boiling points of covalent hydrides plotted against their period numbers.

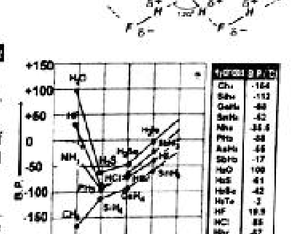


Figure: Graph between boiling points and period number of groups IVA, VA, VIA and VIIA hydrides

Boiling points of hydrides of Group IV A are lowest among all covalent hydrides.

It is because elements of groups IVA are least electronegative, therefore, they have weakest intermolecular forces among all covalent hydrides e.g., CH_4 has lowest boiling point because it is a very small molecule and its has least polarizability.

- ***The boiling point of NH_3, HF, And H_2O are Highest in Their Respective Series.***

It is because these hydrides have strong electronegativity elements N, F and O, which form hydrogen bonding among their own molecules. Thus, their boiling points are high.

- ***H_2O has High B.P. Than HF, Although F is More E.N. Than O.***

It is because, F atom can make only one H-bond per molecule due to presence of one hydrogen, while H_2O can form two H-bond per molecule because it has two hydrogen atoms and two lone pairs of electrons. Hence, due to presence of strong hydrogen bonding in H_2O, its boiling point is greater than HF.

- ***Boiling point of NH_3 is lower than HF and H_2O.***

NH_3 can form one H-bond per molecule. It is because N has only one lone pair of electron. Also, its electronegativity is lower than O and F. Hence, its boiling point is lower than HF and H_2O.

- ***H_2O is a liquid but H_2S and H_2Se are gases***

In H_2O, strong H-bonding is present which makes it a liquid. In H_2S and H_2Se weak intermolecular forces are present. Thus, H_2S and H_2Se are gases at room temperature.

- ***Boiling point of HBr Is Higher Than HCl***

It is due to bigger size of Br than Cl.

Due to bigger size of Br, HBr has greater polarizability and stronger London forces among its molecules than HCl. Hence, boiling point of HBr is greater than HCl.

The hydrides of fourth period e.g. GeH_4, AsH_3, H_2Se and HBr show greater boiling points than those of third period due to larger size and greater polarizabilities.

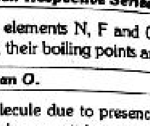
Exercise Q5 (iii):

Water and ethanol can mix easily and in all proportions.

3. Solubility

- ***Both H_2O and Ethyl Alcohol (C_2H_5OH) are Highly Miscible with Each Other***

Substances, which can form H-bond with each other, are highly soluble into each other. Since both H_2O and ethyl alcohol can form hydrogen bonding with each other, therefore, they are miscible with each other in all proportions.



However, larger alcohols are not soluble in water due to non-polar nature of bigger hydrocabon chain in them.

Similarly, small carboxylic acids (RCOOH) are also soluble in H_2O.

- ***Hydrocarbons are insoluble in water***

It is because they are non-polar and cannot develop H-bonding or other attractions with H_2O. Hence, hydrocarbons are insoluble in water.

4. Cleansing Action

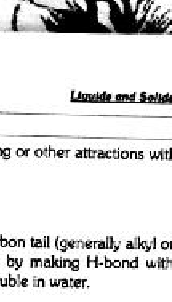
Soaps and detergents are made up of long non-polar hydrocarbon tail (generally alkyl or benzyl) and a polar anion head. In water, the head is stabilized by making H-bond with H_2O, while non-polar tail remains outside H_2O because it is not soluble in water.

Thus, hydrogen bonding helps in cleansing action.

5. H-Bonding in Biological Compounds and Food Materials

H-bonding is very important in living organisms.

- ***Large Protein molecules in living organisms are stabilised due to H-bonding.***



Many fibrous proteins e.g. horn, nail, skin, feather, hair etc. are composed of long chains of amino acids. These chains are coiled around each other and form a spiral. This spiral is called helix. Such helix may either be right handed or left handed. In right handed helix groups like NH and C=O are vertically adjacent to one another and they form H-bonds. These hydrogen bonds link one spiral to the other.

X-ray analysis have shown that on the average there are 3.6 amino acids for each turn of the helix.

- DNA (deoxyribonucleic acid) occurs in cells.

It consists of two spiral chains which are coiled about each other on a common axis and form double helix. This is 18-20 A° in diameter. They are linked together by hydrogen bonding between their subunits.

6. H-Bonding in Paints and Dyes

The adhesive nature of certain paints and dyes is also due to H-bonding with the surfaces.

Similarly, sticky action of Glue and Honey is also due to H-bonding.

7. Food Material

Food material such as carbohydrates e.g. glucose, fructose and sucrose are also stabilized due to H-bonding. All these contains OH group which produce H-bonding.

8. Clothing

Both natural and artificial fibres have rigidity and tensile strength due to H-bonding.

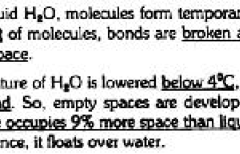
9. Structure of Ice

H_2O has tetrahedral electronic structure.

Ice Floats on water: In liquid H_2O, molecules form temporary H-bond with each other. It is because due to movement of molecules, bonds are broken and reformed. Hence there is less regularity and less free space.

However, when temperature of H_2O is lowered below 4°C, its molecules become regular and form permanent H-bond. So, empty spaces are developed in-between the molecules and its volume increases. Ice occupies 9% more space than liquid water. Thus, density of ice becomes less than water. Hence, it floats over water.

Similarity between structure of Ice and diamond: The structure of ice is just like that of a diamond because each atom of carbon in diamond is at the centre of tetrahedron just like the oxygen of water molecule in ice. It has hexagonal structure with large empty spaces.



Application of low density of ice in cold climates: Density of ice is less than water. Therefore, in cold climate, when temperature falls below 4°C, cold water being lighter comes to the surface and freezes to ice. Thus, an insulating layer of ice is formed above warm water. This layer of ice prevents further heat loss from underneath water. Thus, it protects aquatic life from cold.

EVAPORATION

The spontaneous change of a liquid into vapours is called evaporation.

It continuous at all temperatures.

Explanation

According to kinetic molecular theory, molecules of liquid posses kinetic energy. All the molecules do not have same K.E. Some molecules have K.E. higher than the average value. When such type of molecules come to the surface of liquid, these overcome the intermolecular force and thus escape from the surface of liquid as vapours. This is called evaporation.

In an open container, at constant temperature evaporation continuous at the same rate until all the liquid is converted into vapour. Evaporation continuous at all temperatures.

Factors Affecting the Rate of Evaporation

The rate of evaporation of a liquid depends upon the following factors.

1. Strength of Intermolecular Forces

Different liquids evaporate at different rates.

Stronger the intermolecular force, Lower will be the rate of evaporation and vice versa

e.g. at the same temperature, rate of evaporation of gasoline (petrol) is more than water. Because petrol has weaker London forces.

Similarly rate of evaporation of water is lower than ether. Because in water strong hydrogen bonding is present.

2. Temperature

Increase in temperature increases the rate of evaporation and vice versa.

It is because; increase in temperature increases the number of molecules having K.E. higher than the average value. Thus more molecules are escaped from the surface of liquid, Hence rate of evaporation increases.

3. Surface Area

Larger the surface area, higher is the rate of evaporation and vice versa. It is because, more number of molecules escape from larger surface area. That is why expanded clothes are dried earlier than unexpanded clothes.

Exercise Q12: Explain the following with reason. *(i) Evaporation causes cooling*

i. Evaporation Causes Cooling

Temperature is the measure of average kinetic energy (K.E.) of the particles of a substance. Greater the K.E. higher is the temperature.

When particles having high K.E. escape from the surface of liquid, the average K.E. of the remaining particles decreases. So, temperature of the liquid decreases. As the evaporation continuous, liquid absorbs more and more heat from the surroundings, therefore, temperature of the surrounding also decreases. Hence, evaporation causes cooling.

Exercise Q12: Explain the following with reason.

(vi) Dynamic equilibrium is established during evaporation of a liquid in a closed vessel.

VAPOUR PRESSURE

The pressure exerted by the vapours of a liquid, in equilibrium with the liquid, at a given temperature is called vapour pressure of a liquid.

Explanation

When a liquid is placed in a closed container, then, due to evaporation, molecules leave the surface of liquid, and change into the vapour state. Some of these vapours, on colliding with other vapours, lose a part of their K.E. and are returned to the liquid state. This is condensation process.

Initially the rate of evaporation is higher than the rate of condensation. After sometime, when the space above the liquid becomes saturated with vapours, evaporation rate becomes equal to condensation rate and a dynamic equilibrium is established in the system.

i.e. liquid $\rightleftharpoons$ vapours

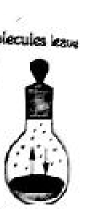


Figure: Establishment of dynamic equilibrium between liquid and its vapours

Like gas, vapours of liquid also collide with the walls of container and exert pressure. This pressure at equilibrium is called vapour pressure of the liquid.

The vapour pressure is independent of the amount and surface area of the liquid.

The evaporation is faster from larger surface area. However, returning molecules also have larger area to return. Thus, condensation is also faster. So, number of molecules per unit surface area remain same. Thus, vapour pressure is independent of amount and surface area of the liquid.

Factors affecting vapour pressure of a liquid

Following factors affect the vapour pressure of a liquid.

(i) intermolecular forces (ii) Temperature

(i) Intermolecular Forces

Stronger the intermolecular forces lower will be the vapour pressure of a liquid and vice versa.

Example 1:

At 35°C H_2O with strong intermolecular hydrogen bonding has low vapour pressure (43 mm of Hg) than ether (442 mm of Hg) in which no hydrogen bonding is present.

Table 4.3 Vapour Pressure of some substances at 20°C

Name of compound	Vapour pressure (torr)
Isopentane	580
Ethyl ether	442.2
Chloroform	170
Carbon Tetrachloride	87
Water	43.9
Mercury	0.012
Glycerol	0.00016

Example 2:

Isopentane has the high vapour pressure due to weak London forces, while glycerol has the low due to strong hydrogen bonding.

(ii) Temperature

Increase in temperature increases the vapour pressure of a liquid and vice versa.

It is because at high temperature, K.E. of molecules increases, therefore, evaporation increases. Hence, vapour pressure increases.

Example:

vapour pressure of H_2O increases from 4.579torr to 9.209 torr from 0°C to 10°C, but it increases from 527.8 torr to 760 torr from 90°C to 100°C

The rate of change of vapour pressure with temperature is given by Clausius–Clapeyron equation.

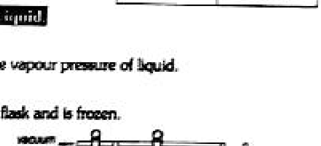
Table 4.4 Vapour pressure of water at different temperatures

Temperature (°C)	Vapour Pressure (torr)
0	4.579
10	9.209
20	17.54
30	31.82
37	47.07
40	55.32
50	92.51
60	149.4
70	233.7
80	355.1
90	527.8
100	760.0

Measurement of Vapour Pressure of a Liquid

Manometric Method

- This method is used to determine accurate vapour pressure of liquid.
- Apparatus is set as shown in the fig.
- Pure liquid is placed in the round bottom flask and is frozen.
- Air above the liquid is removed with a vacuum pump.
- Frozen liquid is remelted to release the entrapped air.
- Liquid is again frozen and air above it is again removed. This process is repeated till all the air is removed.



Measurement of vapour pressure of liquid by manometric method

- The flask is then kept in a thermostat at a temperature at which vapour pressure of the liquid is to be determined.
- The vapours of the liquid pushes the mercury column in the manometer. After sometimes height of mercury in both limbs of manometer becomes constant.
- The vapour pressure of the liquid is given as

$$P = P_{atm} + \Delta h$$

where P = pressure of the liquid, P_{atm} = atomospheric pressrure, and

Δh = difference in height of Hg in manometer.

BOILING POINT

The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure or some other external pressure is called boiling point of a liquid.

Explanation

The vapour pressure of a liquid increases with increase in temperature. When a liquid is heated its vapour pressure goes on increasing until it becomes equal to the external pressure. At this temperature, liquid starts boiling. This is the boiling point of liquid.

The amount of heat required to vaporize one mole of a liquid at its b.p. is called Molar heat of vaporization.

At boiling point bubbles continuously, come out of the boiling liquid. It is because, bubbles formed in the interior of liquid have higher Internal P than atmospheric pressure. Thus, the bubble come out of the liquid and burst upon the surface.

Table: Boiling Points of some common liquids

Liquids	B.P.(°C)	Liquids	B.P.(°C)
Acetic acid	118.50	Carbon tetrachloride	76.50
Acetone	56.00	Ethanol	78.26
Aniline	184.4	Naphthalene	218.00
Benzene	80.15	Phenol	181.80
Carbon disulphide	46.30	Water	100.00

Effect of intermolecular forces on boiling point

Consider the vapour pressure curves of water, ethyl alcohol, ethylene glycol and diethyl ether.

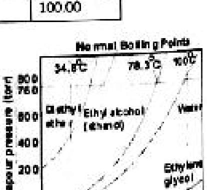


Figure: Vapour pressure of [illegible] common liquids shown as a function of temperature (°C)

- Graph shows, that all the liquids boil at a temperature, at which their vapour pressure becomes equal to 760 torr at sea level.
- At same temperature, curve of diethyl ether starts a 200 torr, while that of water at 4.8 torr. It shows that due to <u>weak intermolecular forces</u>, ether has <u>higher vapour pressure</u> than water.

  Thus, ether boils at lower temperature than water.

  <u>Hence weaker the intermolecular forces, lower will be the boiling point and vice versa.</u>
- <u>The curve shows, that vapour pressures for all liquids increases very rapidly closer to the boiling point of liquids.</u>

Boiling Point and External Pressure

The boiling point of a liquid increases with the increase in external pressure and vice versa.

It is because, at higher external pressure, liquid needs to absorb more heat to equalize its vapour pressure to external pressure hence boiling point is higher. While at lower external pressure liquid needs to absorb less heat, hence boiling point is lower.

e.g., at 760 mm of Hg water boils at 100°C, while
at 1489 mm of Hg water boils at 120°C.

Exercise Q12: Explain the following with reason.

(vii) The boiling point of water is different at Murree hills and at Mount Everest.

- ***Water boils at lower temperature on Murree hills and Mount Everest.***

On Murree hills, external atmospheric pressure is round about 700 mm of Hg, which is lower than normal. Hence, water boils at a lower temperature of 98°C. At further higher altitude, on Mount Everest, external atmospheric pressure is further decreased upto 323 mm of Hg; hence water boils just at 69°C.

Applications of Variation of Boiling Point with Pressure

The variation of boiling point of a liquid with pressure has many applications e.g.; Pressure cooking, vacuum distillation etc.

(1) Pressure Cooking

Principle: *It is based on the fact that increase in external pressure increases the boiling point of a liquid.*

Importance: At higher altitudes, atmospheric pressure is lower than normal (1 atm). Thus water boils at lower temperature e.g.; it boils at 98°C at Murree hills (P=0.92 atm). Thus cooking takes more time.

The boiling point of water can be raised in a pressure cooker. It is a closed container in which vapours are not allowed to escape. Consequently they develop more pressure on the water. Hence, boiling point of water is increased. This helps in cooking the meat & vegetables quickly even at high altitudes.

Exercise Q12: Explain the following with reason.

(viii) Vacuum distillation can be used to avoid decomposition of a sensitive liquid.

(2) Vacuum Distillation

The distillation carried out under reduced pressure is called vacuum distillation.

Principle: *It is based on the fact that decrease in pressure decreases the boiling point of a liquid.*

Importance: Some high boiling liquids cannot be separated by distillation at normal pressure (i.e; 1 atm), since they decompose before reaching their boiling points. e.g.; glycerine boils at

290°C but decomposes before reaching its boiling point. However when the external pressure is reduced to 50 mm of Hg in a vacuum distillation apparatus, it boils at 210°C and therefore can be distilled without decomposition.

ENERGETICS OF PHASE CHANGE

During physical or chemical changes, energy is evolved or absorbed.

Enthalpy Change

The energy change at constant P, in a physical or chemical process is called Enthalpy Change

It is denoted by ΔH. It is expressed in kJ/mol

Three types of enthalpy changes are associated with physical changes

Molar heat of fusion

It is the amount of heat required to convert one mole of a solid into liquid at its melting point.

It is denoted by ΔH_f. It is expressed in kJ/mol

Molar heat of vaporization

It is the amount of heat required to convert one mole of a liquid into vapours at its boiling point.

It is denoted by ΔH_v. It is expressed in kJ/mol

Molar heat of sublimation

It is the amount of heat required to convert one mole of a solid into vapours at its sublimation point.

It is denoted by ΔH_s. It is expressed in kJ/mol

Energy Changes and Intermolecular Attractions

- ***Enthalpy change of a physical change e.g. vaporization can determine the strength of intermolecular forces.***

When a liquid is heated, its temperature goes on increasing until its boiling point is reached. At boiling point the temperature is stopped. Now the heat supplied is used to covert the liquid into vapours by breaking intermolecular forces,

The amount of heat required to convert one mole of liquid into vapours at its boiling point is called molar heat of vaporization (ΔH_v).

Generally, Higher the value of ΔH_v, stronger the intermolecular forces and vice versa. Thus, ΔH_v is actually a measure of strength of intermolecular forces.

Exercise Q12: Explain the following with reason.

(ix) Heat of sublimation of a substance is greater than that of heat of vaporization

- ***Heat of Sublimation is Larger than of Heat of Vaporization***

Heat of vaporization is the amount of heat required to convert liquid into vapours, while, heat of sublimation is the amount of heat required to convert solid into vapours.

Since intermolecular forces are stronger in solids than liquids, therefore, it is difficult to vaporize a solid than a liquid. Hence, heat of sublimation is larger than heat of vaporization.

Substance	ΔH_v kJ/mol
H_2O	+ 40.6
NH_3	+ 21.7
HCl	+ 15.6
SO_2	+ 24.6
F_2	+ 5.9
Cl_2	+ 10.00
Br_2	+ 15.00
I_2	+ 22.00
CH_4	+ 8.60
C_2H_6	+ 15.1
C_3H_8	+ 16.9
C_6H_{14}	+ 30.1

- ***Heat of Fusion of Substances is Less than Heat of Vaporization***

Heat of fusion is defined as the amount of heat required to convert a fixed amount of a solid into liquid at its m.p.

While, heat of vaporization is defined as the amount of heat required to convert a fixed amount of a liquid into its vapours at its boiling point.

To convert solid into liquid, intermolecular forces are not greatly broken, but to convert liquid into vapours, intermolecular forces are largely broken. Therefore, vaporization requires more energy than fusion.

Hence heat of fusion is less than heat of vaporization

Exercise Q12: Explain the following with reason.

(x) Heat of vaporization (or sublimation) of iodine is very high.

- ***I_2 has Higher Heat of Sublimation than its Family Members Substance with greater polarizability has stronger intermolecular forces.***

Polarizability increases with increase in atomic size. Since I_2 has considerably larger size than its family members, therefore, it has greater polarizability and hence strong intermolecular forces. Due to this, it is difficult to vaporize I_2. Hence it has higher heat of sublimation.

- ***Polar Substances have Higher Values of ΔH_v, ΔH_s, ΔH_f***

Polar molecules have stronger intermolecular forces, thus large energy is required to change their physical phase form solid to liquid or liquid to vapours or solid to vapours.

Hence, polar substances have higher values of ΔH_v, ΔH_s, ΔH_f

e.g. H_2O, SO_2, NH_3 etc are polar substances and have considerably higher value of ΔH_v.

Change of State and Dynamic Equilibrium

Reversible process

The process in which both forward and reverse process can occur are called reversible processes

Dynamic equilibrium

The stage of reversible process, at which rate of forward change becomes equal to the rate of backward change is called an equilibrium stage.

Since both changes are occurring simultaneously at equal rate, therefore, this equilibrium is called dynamic equilibrium.

Example:

At $0^{\circ}C$, solid ice exists in dynamic equilibrium with water.

$$\text{ice} \xrightleftharpoons{0^{\circ}C} \text{water}$$

LIQUID CRYSTALS

The intermediate turbid liquid phase of some solids between solid phase and clear liquid phase, showing some properties of liquids and some properties of solids is called liquid crystal.

Discovery

Liquid Crystals were first discovered by an Austrian botanist, F-Reinitzer, in 1888. He was studying an organic compound cholesteryl benzoate. This compound becomes milky at $145^{\circ}C$ and becomes clear at $179^{\circ}C$. On cooling reverse process occurs. This turbid milky phase was called liquid crystal.

Explanation

When a solid is melted, it is converted to a clear liquid.

However, many crystalline solids pass through a turbid liquid phase before finally converting into clear liquid. This turbid phase is called liquid crystal.

A liquid crystalline phase exists between two temperatures, a melting temperature and a clearing temperature.

$$\text{Solid} \xrightleftharpoons{\text{Melting temperature}} \text{Liquid Crystal} \xrightleftharpoons{\text{Clearing temperature}} \text{Clear Liquid}$$

Properties of Liquid Crystals

Their properties are intermediate between crystals and isotropic liquids.

1. These have some degree of order like solids.
2. These have fluidity like liquids.

3. These have properties such as surface tension, viscosity etc. like liquids.
4. These have optical properties of crystalline solids.
5. These are isotropic

Types of Liquid Crystals:

On the basis of ordering of particles, liquid crystals can be divided into various types e.g. nematic, smectic and cholesteric.

Applications

From 1888 to until about 30 years ago, liquid crystals were limited to laboratories. But now these have many applications.

1. Liquid crystals have *excellent electrical and optical properties*
2. Many organic compounds and *biological tissues* behave as liquid crystals
3. Liquid crystals can diffract light. When one of the wavelengths of light is reflected by crystals, they appear coloured. With change in temperature, the distance between layers of molecules of liquid crystals also changes. Hence, colour of reflected light also changes. Thus, liquid crystals can be used as *temperature sensor.*
4. With change in temperature, liquid crystals change colour and give measure of temperature. Thus, these are used to prepare *room thermometer*, for a definite temperature range.
5. This can be used to *find the point of potential failure* in electrical circuits
6. Liquid crystals are used in ***medical diagnosis***. These can be used to locate veins, arteries, infections and tumours. It is because these parts are warmer than surrounding tissues, so they can be detected by using temperature sensitive liquid crystals. This technique is called ***Skin thermography***. It is used

   (i) to detect blockages in veins and arteries.

   (ii) to detect the breast cancer at earlier stage, a layer of temperature sensitive liquid crystal is painted on the surface of breast. The warm tumour shows up in blue colour.

8. These are used in display of electrical devices *(LCD = liquid crystal display)*, such as digital watches, calculators and computers. It is because temperature, pressure and electromagnetic fields can change the weak bonding conditions in crystals, hence give different appearances.
9. In *chromatography*, liquid crystals are used as solvents
10. *Oscillographic and TV display* also use liquid crystal screens.

OBJECTIVE AND SHORT ANSWER QUESTIONS (EXERCISE)

Q.1. Choose the best answer

(i) London dispersion forces are present among the followings

(a) Molecules of water in liquid state
(b) Atoms of helium in gaseous state at high temperature
(c) Molecules of solid iodine
(d) Molecules of hydrogen chloride gas

(Lahore board, 2013) (Gujranwala board, 2014)

(ii) Acetone and chloroform are soluble in each other due to

(a) Intermolecular hydrogen bonding
(b) Dipole-dipole interaction
(c) Instantaneous dipoles
(d) All of the above

(Gujranwala board, 2008) (Bahawalpur Board, 2009) (Sargodha Board, 2009, 2014) (Gujranwala board, 2010) (D.G. Khan Board, 2012) Multan Board, 2012, 2013)

(iii) NH_3 shows maximum boiling point among the hydrides of Vth group element due to *(Rawalpindi board, 2013)*

(a) Very small size of nitrogen
(b) Lone pair present on the nitrogen
(c) Enhanced electronegative character of nitrogen
(d) Pyramidal structure of NH_3

(iv) When water freezes at 0°C, its density decreases due to

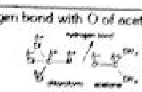
(a) Cubic structure of ice
(b) Empty spaces present in the structure of ice
(c) Change of bond lengths
(d) Change of bong angles

(Faisalabad Board, 2008) (Sargodha Board, 2009, 2012) (D.G. Khan Board, 2012) (Gujranwala board, 2012, 2013)

(v) In order to mention the boiling point of water at 110°C, the external pressure should be *(D.G. Khan Board, 2009) (Multan Board, 2010)*

(a) between 760 torr and 1200 torr
(b) between 200 torr and 760 torr
(c) 765 torr
(d) any value of pressure

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c)	(ii) Ans: (a)
London forces are more prominent in non-polar, bigger sized molecules. I_2 is a non-polar, bigger size molecule; its polarizability is high due to bigger size. Hence, it will have London forces among its molecules.	In chloroform, the three Cl atoms makes the carbon highly δ^+ which in turn makes the H-atom also highly δ^+. On the other hand, in acetone strong E.N. element oxygen is present. Thus, H of chloroform forms hydrogen bond with O of acetone. 
(iii) Ans: (c)	**(iv) Ans: (b)**
Nitrogen has highest electronegativity among group V A elements. Due to this, it can form hydrogen bond among its molecules. Thus, its boiling point is highest among the hydrides of group V A elements.	Ice forms regular hexagonal structure. In this structure, enough empty spaces are present; therefore, volume of ice is increased. Hence, its density is decreased.

(v) Ans: (a)

Boiling point of liquid is directly proportional to the external pressure. At 760 torr, water boils at 100°C. Therefore, boiling point of water will be increased if external pressure is increased. Hence, water boils at 110°C when the external pressure will be between 760 torr and 1200 torr.

Q.2. Fill in the blanks with suitable words.

(i) The polarizability of noble gases _____ down the group and results in the increase in their boiling point.
(ii) _____ is developed in acetone and chloroform and they are mixed together.
(iii) Exceptional weak _____ of HF is due to strong hydrogen bonding present in it.
(iv) The concept of dynamic equilibrium is the ultimate _____ of all reversible systems.
(v) ΔH_v of C_6H_{14} should be _____ than that of C_2H_6.
(vi) During the formation of ice from liquid water there is a _____ increase in volume.
(vii) The rate of increase of vapour pressure for water _____ at high temperature.
(viii) A layer of ice on the surface of water _____ the water underneath for further heat loss.
(ix) Evaporation is a _____ process.
(x) Liquid crystals are used in the display of _____ devices.

Answers:

(i) increases (ii) hydrogen bonding (iii) acidic strength (iv) result (v) greater (vi) 9% (vii) increases (viii) insulates (ix) cooling (x) electrical

Q.3. True or False

(i) Dipole-dipole forces are weaker than dipole-induced dipole forces.
(ii) The ion-dipole interactions are responsible for dissolution of an ionic substance in water.
(iii) The high polarizability of iodine is responsible for its existence in solid form, different from other halogens.
(iv) The strong hydrogen bonding in H_2S makes it different from water.
(v) Hydrocarbons are soluble in water because they are polar compounds.
(vi) The viscosities of liquids partially depend upon the extent of hydrogen bonding.
(vii) The state of equilibrium between liquid state and vapour is dynamic in nature.

(viii) Heat of vaporization of liquids depends upon the intermolecular forces of attraction present between their molecules.

(ix) Ice does not show any vapour pressure on its surface at $-1^{\circ}C$.

(x) Boiling point of a liquid is independent of external pressure.

Answers:
3. (i) False (ii) True (iii) True (iv) False (v) Flase (vi) True (vii) True (viii) True (ix) False (x) Flase

Q.4. *(a) What type of intermolecular forces will dominate in the following liquids?*
(i) Ammonia, NH_3 (ii) Octane, C_8H_{18} (iii) Argon, Ar (iv) Propanone (Acetone) CH_3COCH_3 (v) Methanol, CH_3OH

(i) Ammonia (NH_3)

Nitrogen is a sufficiently strong electronegative element, therefore, N of one molecule will develop H-bond with H of another molecule of NH_3. Hence in NH_3 H-bonding will dominate.

(ii) Octane (C_8H_{18})

Octane is a non-polar molecule. It will not have dipole-dipole interaction or H-bonding. Its molecules will have weak London dispersion forces among themselves.

(iii) Argon (Ar)

Argon is noble gas and is non-polar. It will have London dispersion forces among its molecules. Due to non-polar nature, H-bonding or dipole-dipole interactions will not be present.

(iv) Propanone (Acetone) (CH_3COCH_3)

It has a polar carbonyl group C=O. Due to this group, propanone will develop dipole-dipole interaction.

(v) Methanol (CH_3OH)

In methanol, strong electronegative O is present. Thus O atom of one molecule will form H-bond with H of another methanol molecule.

Thus, methanol chiefly has H-bonding.

(b) Propanone (Acetone) CH_3COCH_3, propanol, $CH_3CH_2CH_2OH$ and butane, CH_3 CH_2 CH_2 CH_3 have very similar relative molecular masses. List them in the expected order of increasing boiling point. Explain your answer?

The boiling points will be in the following order

Propanol >	Propanone	> Butane
$CH_3CH_2CH_2OH$	CH_3COCH_3	$CH_3CH_2CH_2CH_3$
$97^{\circ}C$	$56^{\circ}C$	$0^{\circ}C$

It is because

- Propanol has H-bonding
- Propanone has dipole-dipole interaction
- Butane has weak London dispersion forces

Since H-bonding is stronger than dipole-dipole interaction, which in turn is stronger than London forces.

Q5. Explain the following with reasons.

(i) In the hydrogen bonded structure of HF, which is the stronger bond: the shorter covalent bond or the longer hydrogen bond between different molecules?

Generally shorter bonds are stronger bond.

Further, In HF short covalent bond is formed by overlap of orbitals of H and F. while H-bond is just an electrostatic interaction between different molecules. Hence short covalent bond is stronger than longer H-bond.

(ii) In a very cold winter the fish in garden ponds owe their lives to hydrogen bonding.

In cold winter, when temperature falls below $4^{\circ}C$, cold water being lighter comes to the surface. When temperature is further decreased, cold water freezes to ice. Thus, an insuleting layer of ice is formed above warm water. This layer of ice prevents further heat loss from underneath water. Thus, it saves aquatic life e.g. fishes from cold.

(iii) Water and ethanol can mix easily and in all proportions.

Solved on Page 176

Q6. Briefly consider some of the effects on our lives of if water has only very weak hydrogen bonding present its molecules.

In H_2O if H-bonding is weak, it will have following effects on life.

- The freezing point of water will be lower than $0^{\circ}C$. This will be a serious problem to the life of living things.
- Water acts as thermostat for our earth. With weaker H-bonding, water will not be a thermostat. Thus, there will be large changes in the temperature of the earth.
- Due to weak H-bonding, density of ice will not be less than water. Thus it would be danger for aquatic life.
- With weaker H-bonding, the structures of proteins and DNA would not be satablized.

(b) All gases have a characteristic critical temperature. Above the critical temperature it is impossible to liquefy a gas. The critical temperatures of carbon dioxide and

methane are 31.14°C and -81.9°C, respectively. Which gas has the stronger intermolecular forces? Briefly explain your choice?

The critical temperature of CO_2 is closer to room temperature (i.e. 31.1 °C). It shows that CO_2 is ready to be liquefied around room temperature by applying pressure. However critical temperature of CH_4 is -81.9 °C. It shows that CH_4 must be cooled below this temperature so that it could be liquefied by applying pressure.

Since at room temperature CO_2 is easily liquefied but CH_4 not. Hence, CO_2 has stronger intermolecular forces than CH_4 at the same temperature.

Q7. Three liquids have the properties, mentioned against their names.

	Water	Propanone (Acetone)	Pentane
Molecular Formula	H_2O	C_3H_6O	C_5H_{12}
Relative molecular mass (amu)	18	58	72
Enthalpy of vaporization	41.1	31.9	27.7
Boiling point (°C)	100	56	36

What type of intermolecular force predominates in each liquid:

(i) <u>In water</u>

(ii) <u>In propanone</u>

(iii) <u>In pentane</u>

- H_2O has H-bonding
- Propanone has dipole-dipole interaction
- Pentane has London dispersion forces

(a) What do you deduce about the relative strength of these forces in the liquids? Justify your conclusions.

The order of strength of these forces is

H-bonding>dipole-dipole interaction>London Dispersion forces

Hence, due to strong H-bonding b.p. of H_2O and its ΔH_v is greater than propanone which has dipole-dipole interaction

In pentane weak London dispersion forces are present, therefore, its boiling point and ΔH_v are lower than both H_2O and propanone.

(b) If the liquids are shaken together in pairs.

(i) Which pair would be unlikely to mix?

<u>Water & Pentane</u> will not mix with each other since pentane is non-polar and Water is polar. Therefore they will not have attractions for each other.

(ii) Explain this immiscibility in terms of the forces between the molecules.

H_2O and propanone are polar substances and have H-bonding and dipole-dipole interactions. Hence they attract the molecules of each other. Thus, they mix with each other.

However, pentane is non-polar and has weak London dispersion forces. It can not develop forces with water or propanone molecules, hence, it is immiscible with H_2O and propanone.

(iii) Choose one of the pairs that mix and say whether the enthalpy change on mixing would be positive or negative.

Water and propanone will mix with each other. This mixing is exothermic process and have –ve enthalpy change, because both water and acetone have strong attractions for each other during which energy is released

Q8. Describe the various forces responsible for keeping the particles together in the following elements and compounds and their effects on physical properties making use of the data below:

Substance	Formula	Molar Mass (g mol⁻¹)	M.P (°C)
Neon	Ne	20	-248
Argon	Ar	40	-189
Water	H_2O	18	0
Sodium fluoride	NaF	42	993
Diamond	C	12	3350

- Ne and Ar are noble gases and have weak London dispersion forces. Since Ar is larger in size, therefore, it has greater polarizability than Ne and therefore strong London forces. Hence its m.p. is higher than Ne.
- Water has strong H-bonding, therefore, it will have sufficiently high m.p. than Ne and Ar.
- NaF is an ionic solid. It has cubic crystal structure in which each Na^+ ion is surrounded by six F^- ions and each F^- is surrounded by six Na^+ ions. These ions have strong electrostatic forces. This arrangement gives hardness to NaF crystal.

For melting NaF crystal, large amount of energy is required. Hence, its m.p. is higher than Ne, Ar and H_2O.

- Diamond has network of carbon atoms, which are joined together by strong covalent bonds in a tetrahedral manner.

Due to strong network of C atoms, it is very difficult to separate these atoms from each other. Hence Diamond has higher m.p. than Ne, Ar, H_2O and NaF.

Q9. The boiling points and masses of hydrides of some first row element are tabulated below:

Substance	Boiling Point (K)	Molar Mass (g/mol)
CH_4	109	16
NH_3	240	17
H_2O	373	18

Suggest reasons for the difference in their boiling points in terms of the type of molecules involved and the nature of the forces present between them.

C, N, and O are present in same period of periodic table.

- Of these, C has the least electronegative while O has the highest electronegativity.
- CH_4 is a symmetrical and non-polar molecule. Therefore, it has weak London dispersion forces. Hence, its boiling point is very low
- NH_3 is an unsymmetrical polar molecule. In NH_3, due to high electronegativity of N, it develops H-bonding among its molecule. NH_3 can form one H-bond per molecule. Hence, its boiling point is higher than CH_4
- H_2O is an unsymmetrical polar molecule. In H_2O, strong H-bonding is present due to highest E.N. of oxygen atom. Moreover, water molecules can form two H-bonds per molecule.

Hence, its boiling point is higher than both CH_4 and NH_3.

Q10. Explain the term saturated vapour pressure. Arrange in order of increasing vapour pressure: $1 dm^3$ water, $50 cm^3$ water, $1 dm^3$ of ethanol, $50 cm^3$ ethanol and $50 cm^3$ of ether.

Vapour pressure does not depend on the amount of substance but it depends upon their nature.

Generally, Stronger the intermolecular forces lower will be the vapour pressure and vice versa. Hence order of vapour pressure will be

$50\ cm^3$ of ether > $1\ dm^3$ of ethanol = $50\ cm^3$ of ethanol > $1\ dm^3$ of H_2O = $50\ cm^3$ of H_2O

It is because, that H_2O has strongest H-bonding and it can form two H-bond per molecule, therefore, its vapour pressure is lowest.

Ethanol has somewhat weak H-bonding than H_2O because ethanol can form one H-bond per molecule. Therefore, its vapour pressure is higher than H_2O.

Ether has only weak forces. Hence its vapour pressure is the highest.

Q11. While a volatile liquid standing in a beaker evaporates, the temperature of the liquid remains the same as that of its surroundings. If the same liquid is allowed to vaporized into atmosphere in an insulated flask, its temperature falls below that of its surrounding. Explain the difference in behaviour.

When a liquid is evaporating continuously in an open container, heat from the surrounding enters into the liquid. Hence temperature of liquid remains equal to that of surroundings.

However, if liquid is insulated from surroundings then due to evaporation, its T will fall but no heat will move from surrounding into liquid.

As a result temperature of liquid falls below that of surroundings.

Q12. Explain the following with reason.

(i) Evaporation causes cooling

Solved on Page 179

(ii) Evaporation takes place at all temperatures

(Faisalabad Board, 2007: Bahawalpur Board, 2008: Gujranwala Board, 2010. Lahore Board, 2014)

Molecules of liquids have K.E. at all temperature. Thus, they are continuously moving. They collide with one another. As a result some molecules may get K.E. higher than the average value. Such molecules escape from the liquid surface as vapours. Hence, evaporation takes place at all temperature.

At low temperature, K.E. of molecules is low, therefore, rate of evaporation is also low. However, rate of evaporation increases with increase in temperature.

More or less, evaporation continuous at all temperature.

(iii) Boiling needs a constant supply of heat

(D.G. Khan Board, 2009: Lahore Board, 2010)

Liquid boils at a temperature at which its vapour pressure becomes equal to the external pressure.

Since vapour pressure of a liquid depends on temperature, therefore, vapour pressure of a liquid becomes equal to external pressure only at a specific temperature. To keep liquid boiling, this temperature must be maintained. Thus, a constant supply of heat must be supplied to the boiling liquid.

(iv) Earthenware vessels keep water cool

(Multan Board, 2007. Bahawalpur Board, 2012: Lahore Board, 2012. Gujranwala Board, 2012)

Earthenware pots have small pores. When water is placed in earthenware pots, it evaporates through the pores. Due to continuous evaporation of water from the whole surface of earthenware pots, its temperature decreases. Hence, earthenware vessels keep water cool.

(v) One feels sense of cooling under the fan after bath. OR Why do we feel cooling effect after taking bath.

(Bahawalpur Board, 2008: Gujranwala Board, 2008: Faisalabad Board, 2012: Lahore Board, 2013) (Multan Board, 2009: Bahawalpur Board, 2010: Gujranwala Board, 2013)

Under fan, the rate of evaporation of water from the body is increased. Water vapours take heat from the body and evaporate. As a result one feel's sense of cooling under the fan after bath.

(vi) Dynamic equilibrium is established during evaporation of a liquid in a closed vessel.

Solved on Page 180

(vii) The boiling point of water is different at Murree hills and at Mount Everest.

Solved on Page 183

(viii) Vacuum distillation can be used to avoid decomposition of a sensitive liquid.

Solved on Page 183

(ix) Heat of sublimation of a substance is greater than that of heat of vaporization.

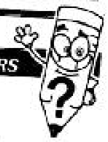
Solved on Page 185

(x) Heat of vaporization (or sublimation) of iodine is very high.

Solved on Page 185

HELLO! Mr. Question here!

OBJECTIVE: Multiple Choice Questions from PAST PAPERS



1. Glycerine decomposes at its: *(Lahore board, 2014)*
   (a) Melting point (b) Boiling point (c) Freezing point (d) Critical point
2. Which of the follwing liquid has highest boiling point: *(Rawalpindi board, 2011)*
   (a) HCl (b) HBr (c) H_2O (d) Br_2
3. Ice occupies more space than liquid water upto: *(Rawalpindi board, 2011)*
   (a) 9% (b) 10% (c) 11% (d) 12%
4. Forces which are present between ions and water molecules are: *(Rawalpindi Board, 2009: Gujranwala board, 2009)*
   (a) Dipole-induced dipole forces (b) Dipole-dipole forces
   (c) Ion-dipole forces (d) London dispersion forces
5. Hydrogen bonding is maximum in: *(Gujranwala board, 2011)*
   (a) HI (b) HBr (c) HCl (d) HF
6. Dipole-induced dipole forces are also called: *(Multan Board, 2011)*
   (a) London Dispersion Forces (b) Debye Forces
   (c) Huckel Froces (d) Electrostatic Forces
7. Liquid crystals are used as solvent in: *(Multan Board, 2011)*
   (a) Solvent extraction (b) Crystallization
   (c) Filtration (d) Chromatography
8. Cholesteryl benzoate turn into milky liquid at *(Rawalpindi Board, 2013)*
   (a) 144°C (b) 145°C (c) 146°C (d) 147°C
9. Ice occupied more space than liquid water *(Lahore Board, 2010)*
   (a) 9% (b) 10% (c) 11% (d) 12%
10. The boiling point of higher alkanes are greater than those of lower alkanes due to the reasons that *(Faisalabad Board, 2010)*
    (a) Higher alkanes have greater number of atoms.
    (b) The polarizeability of higher alkanes are greater
    (c) Higher alkanes have zigzag structure.
    (d) Higher alkanes have greater hydrogen bonding
11. The strongest acid among halogen acid is *(Bahawalpur Board, 2010)*
    (a) HF (b) HCl (c) HBr (d) HI
12. Water has maximum density at *(Faisalabad Board, 2011)*
    (a) 4.0°C (b) 0°C (c) 100°C (d) 10°C
13. At Muree hills water boils at: *(Lahore Board, 2007)*
    (a) 98°C (b) 100°C (c) 0°C (d) 50°C

14. The volume of ice increases than liquid water by (Faisalabad Board, 2007)
(a) 5% (b) 9% (c) 12% (d) 15%

15. Boiling point of H_2O at Mount Everest would be (D.G. Khan Board, 2010)
(a) 98°C (b) 100°C (c) 101°C (d) 69°C

16. Liquid hydrocarbon is (Lahore Board, 2011)
(a) Methane (b) Propane (c) Ethane (d) Hexane

17. The distillation of liquid under reduced pressure is called? (Sargodha Board, 2013)
(a) destructive distillation (b) vacuum distillation
(c) fractional distillation (d) simple distillation

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(b)	2	(c)	3	(a)	4	(c)	5	(d)
6	(a)	7	(d)	8	(b)	9	(a)	10	(b)
11	(d)	12	(a)	13	(a)	14	(b)	15	(d)
16	(d)	17	(b)						

SUBJECTIVE QUESTIONS FROM PAST PAPERS

INTERMOLECULAR AND INTRAMOLECULAR FORCES, DIPOLE-DIPOLE FORCES

Short Questions

(1) *Intermolecular forces are stronger than intramolecular forces. Why?* (Sargodha Board, 2010)
(2) *Define Dipole-Dipole forces and ion-dipole forces.* (Rawalpindi Board, 2010)
(3) *London dispersion forces are weaker than dipole – dipole forces. Why?* (Faisalabad Board 2008) **OR** *Dipole-dipole forces are stronger than London dispersion forces.* (Multan Board 2009)

Long Questions

(1) *What are intermolecular forces? Name the four types of these forces and explain any one* (Rawalpindi Board, 2009)
(2) *What are intermolecular forces? Write the names of different types of their forces and explain instantaneous dipole-induced dipole forces.* (Faisalabad Board, 2012)
(3) *Define Debye forces, Amorphous solids, Allotropy and Hydrogen bonding.* (Lahore Board 2007)

LONDON DISPERSION FORCES, FACTORS AFFECTING LONDON DISPERSION FORCES

Short Questions

(1) *What are London dispersion forces (or interactions)?* (Faisalabad Board, 2009: Sargodha Board, 2007, 2009: Sargodha Board, 2010)
(2) *How the increase of polarizability down the group in noble gases is responsible for the increase in melting and boiling points?* (D.G. Khan Board, 2011) OR *Boiling point increases from He to Rn in VIII group. Why?* (Bahawalpur Board, 2011) OR *Why the boiling points of noble gases increase down the group?* (Gujranwala Board, 2014)
(3) *Melting points and boiling points of halogens increases down the group. Explain it.* (Rawalpindi Board, 2007: Faisalabad Board, 2009)
(4) *Why the melting and boiling points of alkanes increase with increase in molar mass?* (Lahore Board, 2007: Sargodha Board, 2009: Rawalpindi Board, 2009)
(5) *Why ethane (C_2H_6) is a gas whereas hexane (C_6H_{14}) is a liquid at S.T.P.?* (D.G. Khan Board, 2010: Azad Kashmir Board, 2012)

Long Questions

(1) *Write a note on factors affecting London Forces.* (Sargodha Board, 2013)

HYDROGEN BONDING AND ITS APPLICATIONS

Short Questions

(2) *H-bonding is present in chloroform and acetone. Justify.* (Multan Board, 2009)
(3) *Why HF is a weaker acid than HCl* (Multan Board, 2008: Lahore Board, 2009: D.G. Khan Board, 2012: Rawalpindi Board, 2013)
(4) *Why boiling point of H_2O is greater than HF?* (Sargodha Board, 2013: Lahore Board, 2014)
(5) *Water is liquid at room temperature but H_2S is a gas. Give reason.* (Bahawalpur Board, 2008: Lahore Board, 2009: Gujranwala Board, 2011: Rawalpindi Board, 2009, 2011: Multan Board, 2012)
(6) *Water and ethanol can mix in all proportions, give reason.* (Lahore Board, 2013) OR *Lower alcohols are water soluble but corresponding alkanes are insoluble in water. Why?* (Lahore Board, 2007)
(7) *Write down two applications of hydrogen bonding.* (Rawalpindi Board, 2012)
(8) *Polar compounds are soluble in a polar solvents. Justify the statement.* (Bahawalpur Board, 2009)
(9) *Ice floats on water. Justify it.* **OR** *Ice occupies more space then water, give reason.* **OR** *How sea life survives under frozen sea? OR Density of ice is less than liquid water, explain with reason.* (Multan Board, 2007: Faisalabad Board, 2008, 2011, 2013: Lahore Board, 2009, 2013: Sargodha Board, 2009, 2011: Multan Board, 2010: Rawalpindi Board, 2010: D.G. Khan Board, 2012)
(10) *Water freezes from surface to the down direction in ponds and lakes. Explain with reason.* (Bahawalpur Board, 2011) **OR** *Lower density of ice than water has got significance. Comment.* (Multan Board, 2008)
(11) *Water freezes from surface to the downward direction in ponds and lakes. Explain why?* (D.G. Khan Board, 2010)

Long Questions

(1) *Define hydrogen bonding. How does it explain the indicated properties of following substances?* (Lahore Board, 2010)

(2) Explain hydrogen bonding in NH_3, H_2O and HF, how it is helpful in explaining the structure of ice. **(Lahore Board, 2011)**

(3) What is hydrogen bonding, Explain role of hydrogen bonding in food and biological material. **(Sargodha Board, 2011)**

(4) How does hydrogen bonding explain the formation of ice and its lesser density than liquid water. **(Gujranwala Board, 2012)**

EVAPORATION, VAPOUR PRESSURE

Short Questions

(1) How the rate of evaporation depends on the surface area? **(Lahore Board, 2009)**

(2) Evaporation of a liquid causes cooling. Explain. **(D.G. Khan Board, 2007, 2008: Multan Board 2010: D.G. Khan Board, 2012: Sargodha Board, 2007, 2014: Faisalabad Board, 2009: Lahore Board 2010, 2011, 2014)**

(3) Define evaporation and vapour pressure. **(Faisalabad Board, 2010) Ans: Take definat**

(4) Define vapour pressure of a liquid. **(Faisalabad Board, 2009)**

(5) Define vapour pressure. Write down two factors that affect vapour pressure of a liquid. **(Rawalpindi Board, 2011)**

(6) Why the vapour pressure of water. Ethyl alcohol and diethyl ether are different from each other at 0°C. **(Rawalpindi Board, 2007)**

Long Questions

(1) Define Vapour pressure. Write a method for determination of vapour pressure of a liquid. **(Bahawalpur Board, 2009: Multan Board, 2013: Sargodha Board, 2013, 2014)**

(2) How vapour pressure is measured by Manometer method. **(Faisalabad Board, 2007: Gujranwala Board, 2009, 2011: D.G. Khan Board, 2012: Multan Board, 2012)**

BOILING POINT, EFFECT OF EXTERNAL PRESSURE ON BOILING POINT

Short Questions

(1) Define boiling point **(Faisalabad Board, 2012) OR** Define boiling point. How it is affected by external pressure? **(Rawalpindi Board, 2010)**

(2) The boiling point of water is different at Murree Hills and at Mount Everst. Explain with reason. **(Faisalabad Board, 2007, 2010: Sargodha Board, 2013) OR** Water boils at lower temperature on Hilly areas than on plane areas. Why? **(Bahawalpur Board, 2010)**

(3) Explain the working of pressure cooker. **(Faisalabad Board, 2011)** OR Food can be cooked quickly in Pressure Cooker. Explain with reason. **(Sargodha Board, 2011, 2014)**

(4) Vacuum distillation can be used to avoid decomposition of a sensitive liquid. Explain **(Bahawalpur Board, 2012: Lahore Board, 2012) OR** What is the importance of vacuum distillation? **(Gujranwala Board, 2009, 2011)**

(5) Why different liquids possess different boiling points? **(Multan Board, 2013)**

Long Questions

(1) What is boiling point? What is the effect of external pressure on boiling point? Why the temperature, of a liquid remains constant at boiling point although heat is continuously supplied? **(Lahore Board, 2013)**

(2) What is the effect of external pressure on boiling point of a substance? Give example **(Multan Board, 2012)**

MOLAR HEATS OF FUSION, VAPORIZATION, SUBLIMATION

Short Questions

(1) What are molar heat of fusion and molar heat of sublimation. **(Sargodha Board, 2010)**

(2) Define molar heat of vaporization and molar heat of fusion. **(Gujranwala Board, 2010)**

(3) Define molar heat of vaporization with one example. **(Rawalpindi Board, 2009)**

(4) Why heat of sublimation of a substance is greater than that of heat of vaporization **(Sargodha Board, 2012: Faisalabad Board, 2010, 2013: Rawalpindi Board, 2013)**

(5) Heat of sublimation of iodine is very high. Explain with reason. **(D.G. Khan Board, 2007: Rawalpindi Board, 2010: Lahore Board, 2012: Gujranwala Board, 2012, 2013: Lahore Board, 2014)**

(6) Gasoline evaporates much faster than water. Give reason. **(Gujranwala Board, 2014)**

(7) Why the heat of vaporization of water is greater than that of CH_4 **(D.G. Khan Board, 2011)**

(8) Why heat of vaporization of hexane is greater than that of ethane. **(Sargodha Board, 2007)**

(9) Steam causes more severe burns than does the boiling water. **(Gujranwala Board, 2010)**

LIQUID CRYSTALS AND THEIR APPLICATIONS

Short Questions

(1) How liquid crystals act as temperature sensors? **(Lahore Board, 2007: Multan Board, 2013)**

(2) How liquid crystals are used as a locator of tumors? **(D.G. Khan Board, 2009)**

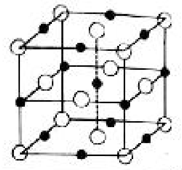
(3) Give uses (or applications) of liquid crystals. **(D.G. Khan Board, 2007: Rawalpindi Board, 2009: Multan Board, 2012: Lahore Board, 2011, 2013: D.G. Khan Board, 2012: Faisalabad Board, 2013: Sargodha Board, 2013); Ans:** All uses are given below. Generally, two or four uses are asked in short question.

Long Questions

(1) What are liquid crystals? Give their two uses (or three uses) in daily life. **(Faisalabad Board, 2009, 2011: Gujranwala Board, 2010: D.G. Khan Board, 2009: Azad Kashmir Board, 2012: Lahore Board, 2014)**

(2) Give four uses of liquid crystals. **(Gujranwala Board, 2008: Sargodha Board, 2009)**

(3) Define liquid crystals. Discuss important uses of liquid crystals **(Sargodha Board, 2012: Gujranwala Board, 2013: Lahore Board, 2014)**



INTRODUCTION

Exercise Q.4:

What are solids? Give general properties of solids. How do you differentiate between crystalline solids and amorphous solids?

Solid

It is the state of matter, which has the strongest intermolecular forces, definite shape and definite volume.

In solids atoms, ions and molecules are held together by strong cohesive forces and these cannot move at random.

Most of the solids exist in crystal form.

Types of Solids **(Classification of solids on the basis of Regularity of Particles)**

On the basis of regularity of solid particles, these are divided into two types.

1. Crystalline solids 2. Amorphous solids

1. Crystalline solids

The solids in which atoms, ions or molecules have regular, three-dimensional arrangement are called crystalline solids.

Examples:

NaCl, Diamond etc.

2. Amorphous solids

The solids in which atoms ions, or molecules do not have a regular orderly arrangement are called amorphous solid.

These are called pseudo solids.

Properties

1. These have random structure.
2. These have short range order like liquids.
3. They don't posses repetitive structure of crystals.
4. They may have hardness and elasticity.

5. They do not posses sharp melting point.
6. These have indefinite heats of fusion.

Examples:

Glass, Rubber, Plastics, Glue etc.

NOTE:

- ***Cyrstallites:*** In amorphous solids long range order is absent. These solids have areas of short-range order in their structure. These areas are called *crystallites*.
- ***Super-Cooled Liquids:*** Many crystalline solids can be changed into amorphous solids by melting and then cooling rapidly. In this way, particles can not arrange themselves regularly. Thus, they have definite volume and shape but arrangement of particles is not regular. Hence, these are also called *super cooled liquids*.

Difference between Crystalline and Amorphous Solids

	Crystalline Solids		Amorphous Solids
1	These have definite geometric shape in which atoms, ions or molecules have a regular, and repetitive, three dimensional arrangement.	1	These do not have definite geometric shape.In these atoms ions,or molecules have a random or non-repetitive three dimensional arrangement.
2	These have sharp melting points.	2	These do not have sharp melting points.
3	These have definite heats of fusion	3	These have indefinite heats of fusion.
4	These are anisotropic.	4	These are isotropic and resemble liquids.
5	These are called true solids.	5	These are called pseudo solids.
6	Examples: NaCl , diamond , KCl etc.	6	Examples: Glass , Rubber etc.

Exercise Q.6 (a):

Define unit cell. What are unit cell dimensions? How the idea of crystal lattice is developed from the concept of unit cell?

UNIT CELL

The smallest part of the crystal lattice, showing all the characteristic features of the whole crystal is called a unit cell.

Unit Cell dimensions or Crystallographic Elements

unit cell

Figure: [illegible] crystallographic elements specify the size and shape of unit cell

- A unit cell is identified by the length of its faces i.e., sides (unit cell lengths) and the angles between these faces (unit cell angles).
- There are three unit cell lengths represented by ***a***, ***b***, c and three unit cell angles denoted by α, β, γ as shown in figure.

Angle between sides 'b' and 'c' is 'α',

Angle between sides 'a' and 'c' is 'β',

Angle between sides 'a' and 'b' is 'γ'

- All the six parameters of a unit cell are called unit cell dimensions or crystallographic elements.

Importance of Unit Cell

- Thus complete information of crystal is present in its unit cell.
- If structure of a unit cell is known, then structure of whole crystal can be made by repeating it.

There are seven different types of unit cells depending on the length of faces and angles. So, there are seven types of crystal lattice/crystal systems.

Crystal Lattice

It is an array of points, representing atoms, ions or molecules of a crystal, arranged at different sites in three-dimensional space.

Explanation

In crystals, particles have definite positions. These are represented by points in a crystal. These points are called lattice points or lattice sites. This three dimensional arrangement of points in a crystal is called crystal lattice or space lattice. e.g. NaCl

Figure: Cubic crystal lattice

Exercise Q.6 (b):

Explain seven crystal systems and draw the shapes of their unit cells.

CRYSTALS AND THEIR CLASSIFICATION

The group of crystals whose shapes are built up by only one type of unit cells are called crystal systems.

There are seven different types of crystal systems.

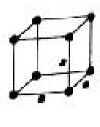
1. Cubic System

All the sides are equal

$a = b = c$

All the angles are of 90°

$\alpha = \beta = \gamma = 90°$



Examples

Fe, Cu, Ag, Au, NaCl, NaBr, diamond etc.

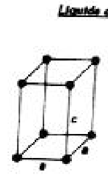
2. Tetragonal System

Out of three, two sides are equal

$a = b \neq c$

All the angles are of 90°

$\alpha = \beta = \gamma = 90°$



Examples

Sn, SnO_2, MnO_2, NH_4Br etc.

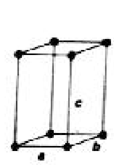
3. Orthorhombic System

All the sides are unequal

$a \neq b \neq c$,

All the angles are of 90°

$\alpha = \beta = \gamma = 90°$



Examples

Iodine, Rhombic sulphur, K_2SO_4, $BaSO_4$ etc.

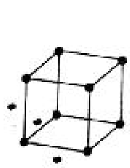
4. Trigonal Or Rhombohedral System

All the sides are equal

$a = b = c$

All the angles lie between 90° and 120°

$\alpha = \beta = \gamma \neq 90°$



Examples

Bi, Al_2O_3, $NaNO_3$, KNO_3 etc.

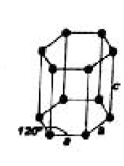
5. Hexagonal System

Out of three, two sides are equal

$a = b \neq c$

Two angles are of 90° and third is of 120°

$\alpha = \beta = 90°$ and $\gamma = 120°$



Examples

Graphite, ZnO, CdS, Ice, Zn, Cd etc.

6. **Monoclinic System**

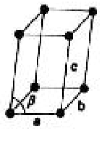
All the sides are unequal

$a \neq b \neq c$

Two angles are of 90°

and third one is greater than 90°

$\alpha = \gamma = 90°$ and $\beta > 90°$



Examples

Sugar, Monoclinic Sulphur, $Na_2SO_4.10\,H_2O$, Borax etc.

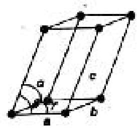
7. **Triclinic System**

All the sides are unequal

$a \neq b \neq c$

All the angles are unequal

$\alpha \neq \beta \neq \gamma \neq 90°$



Examples

H_3BO_3, $CuSO_4.\,5H_2O$, $K_2Cr_2O_7$ etc.

TABLE 4.7 Seven Crystal Systems

Sr. No	Crystal system	Axes	Angles	Exemples
1.	Cubic	$a=b=c$	$\alpha=\beta=\gamma=90°$	Fe, Cu, Ag, NaCl, NaBr, Diamond
2.	Tetragonal	$a=b\neq c$	$\alpha=\beta=\gamma=90°$	Sn, SnO_2, MnO_2, NH_4Br
3.	Orthorhombic	$a\neq b\neq c$	$\alpha=\beta=\gamma=90°$	Iodine, Rhombic sulphur, $BaSO_4$
4.	Rhombohedral or Trigonal	$a=b=c$	$\alpha\neq\beta\neq\gamma\neq 90°$	Bi, Al_2O_3, $NaNO_3$, KNO_3
5.	Hexagonal	$a=b\neq c$	$\alpha=\beta=90°, \gamma=120°$	Graphite, ZnO, CdS, Ice, Zn, Cd
6.	Monoclinic	$a\neq b\neq c$	$\alpha=\gamma=90°\ \beta\neq 90°$	Suger, Sulphur, Borax, $Na_2SO_4.10H_2O$
7.	Triclinic	$a\neq b\neq c$	$\alpha\neq\beta\neq\gamma\neq 90°$	H_3BO_3, $K_2Cr_2O_7$, $CuSO_4.5H_2O$

Exercise Q.5 (a)

Explain the following properties of crystalline solids. Give three examples in each case.

(i) Anisotropy (ii) Cleavage (iii) Habit of a crystal (iv) Isomorphism (v) Transition temperature (vi) Symmetry (vi) Growing of a crystal (vii) Polymorphism

PROPERTIES OF CRYSTALLINE SOLIDS

1. **Geometrical shape**

Crystalline solids have definite, regular three dimensional arrangement of particles.

Each crystal has definite faces (sides) and definite angles (interfacial angles) between the faces.

For a given crystal, the interfacial angles, at which the surfaces intersect, are always the same no matter in which shape they are grown. The faces and angles of crystals are not changed even if it is ground to a fine powder.

2. **Melting point**

Crystalline solids have definite melting point and can be identified by this. Thus crystals have definite heats of fusion.

3. **Cleavage and Cleavage Plane**

The breaking of crystalline solids into smaller identical crystals due to external pressure is called cleavage.

The plane in which a crystalline solid can be broken into smaller identical crystals is called cleavage plane.

The cleavage planes are inclined to one another at a particular angle for a crystalline solid. The angle is different for different solids.

4. **Anisotropy**

Some of the crystals show variation in physical properties depending upon the direction. Such properties are called anisotropic properties and the phenomenon is called anisotropy.

A substance, which has this property, is called an anisotrope.

Crystals show the property of anisotropy. It is because crystals have different arrangement of particles in different directions.

Examples:

In crystals, electrical conductivity, thermal conductivity, co-efficient of thermal expansion and refractive index are anisotropic properties.

Electrical conductivity of graphite is greater in one direction than other. It is because in graphite mobile electrons can move easily parallel to its layers rather than perpendicular to its layer.

Cleavage itself is an anisotropic behaviour.

- ***The properties, which do not depend upon the direction, are called isotropic properties.*** e.g., melting point etc.
- The substance which posses isotropic property is called isotrope.

5. **Symmetry**

The repetition of faces, angles and edges when a crystal is rotated by 360° along its axis is called symmetry.

Crystals have various types of symmetry elements. e.g. centre of symmetry, plane of symmetry, axis of symmetry etc.

6. Habit of crystals

The shape in which a crystal usually grows is called habit of a crystal.

e.g.; when a saturated solution of NaCl is cooled, cubic crystals of NaCl are formed. Thus NaCl has cubic habit.

Crystals are obtained either by cooling its saturated solution or by slow cooling of liquid substances. These are formed by growing in various directions. In particular conditions, shape of growing crystal is not changed. However, if conditions are changed then shape of the crystal may also change.

e.g. Cubic crystal of NaCl becomes needle like when 10% urea is present in solution as impurity.

7. Isomorphism

The phenomenon in which two different substances exist in the same crystalline form is called isomorphism.

These different substances are called isomorphs of each other.

- Isomorphous substances have different physical and chemical properties.
- The formula of isomorphous substances shows that they generally have same ratio of their atoms.
- A crystal structure depends only on the number of atoms and their way of combination. It does not depend on chemical nature of atoms.
- Isomorphous substances crystallize together in all proportions in a homogeneous mixture.

Examples:

[illegible]	[illegible]	[illegible]
$NaNO_3$, KNO_3	Rhomobohedral	1 : 1 : 3
K_2SO_4, K_2CrO_4	Orthorhombic	2 : 1 : 4
$ZnSO_4$, $NiSO_4$	Orthorhombic	1 : 1 : 4
NaF, MgO	Cubic	1 : 1

- The structure of negative ions like NO_3^- and CO_3^{2-} are same. Both are triangular planar.
- Similarly the Structure of SO_4^{2-} and CrO_4^{2-} are also same. Both are tetrahedral.

8. Polymorphism

The phenomenon in which a substance exists in more than one crystalline form is called polymorphism.

- The substance, which exists in more than one crystalline form, is called polymorphic.
- Different crystalline forms of a substance are called polymorphs.
- Polymorphs of a substance have same chemical properties
- Polymorphs have different physical properties. It is due to different structural arrangement of their particles.

Examples:

- $AgNO_3$ exists as Rhombohedral, Orthorhombic
- $CaCO_3$ exists as Trigonal and orthorhombic

Difference between Isomorphism and Polymorphism

	Isomorphism		Polymorphism
1	Different substances exist in same crystalline forms.	1	Same substance exists in two crystalline form
2	Isomorphous substances have different physical and chemical properties	2	Polymorphic forms have same chemical properties but different physical properties
3	Isomorphous substances cannot be inter-converted	3	Polymorphic forms can be inter-converted
4	Isomorphic forms have different formula units	4	Polymorphic forms have same formula unit
5	Examples Both MgO and NaF are isomorphous	5	Examples $CaCO_3$ exists in trigonal and orthorhombic form

9. Allotropy

The phenomenon in which an element exists in more than one crystalline form is called allotropy.

Different crystalline forms of an element are called allotropes or allotropic forms

Examples:

- Carbon can exist in graphite (Hexagonal) and diamond (cubic) forms.
- Sulphur can exist in Rhombic and Monoclinic forms.
- Tin (Sn) can exist as grey tin(cubic) and white tin(tetragonal)

10. Transition Temperature

The temperature at which two crystalline forms of the same substance can co-exist in equilibrium with each other is called transition temperature.

Examples:

Sulpher (rhombic)	$\underset{}{\overset{95.5^\circ C}{\rightleftharpoons}}$	Sulpher (monoclinic)
Grey Tin (cubic)	$\overset{13.2^\circ C}{\rightleftharpoons}$	White Tin (Tetragonal)
KNO_3(orthorhombic)	$\overset{128^\circ C}{\rightleftharpoons}$	KNO_3(rhombohedral)
$Na_2SO_4.10H_2O$(hydrated form)	$\overset{32.38^\circ C}{\rightleftharpoons}$	Na_2SO_4(anhydrous form) + $10H_2O$
$Na_2CO_3.10H_2O$(higher hydrated form)	$\overset{32.02^\circ C}{\rightleftharpoons}$	$Na_2CO_3.7H_2O$(lower hydrated form) $+3H_2O$

- At this temperature, one crystalline form of a substance changes into other.
- Above and below this temperature, only one form exists.
- The transition temperature of the allotropic form of an element is always less than its melting point.

CLASSIFICATION OF SOLIDS

(On the basis of forces present in the crystal)

Crystal have been classified into four types on the basis of forces present between atoms, ions or molecules in them. These forces are also called cohesive forces. These forces may be chemical bonds or some other interactions.

There are four types of crystalline solids on the basis of nature of forces present in them.

A. Ionic solids B. Covalent solids

C. Molecular solids D. Metallic solids

Exercise Q.7 (a):

What are ionic solids? Give their properties. Explain the strucuture of NaCl. Sketch a model to justify that unit cell of NaCl has four formula units in it.

IONIC SOLIDS

The crystalline solids, in which positively and negatively charged ions are held together by electrostatic forces of attractions, are called ionic solids. These forces are also called ionic bonds

Examples:

NaCl, $BaCl_2$, K_2SO_4 etc.

Properties of Ionic Solids

1. These are crystalline solids at room temperature, due to definite arrangement of cations and anions
2. Under normal temperature and pressure, these never exist as liquids or gases.
3. These are stable compounds. In ionic crystals, ions are held together by strong electrostatic forces, which are difficult to break. Hence these are stable.

4. These have high melting point and boiling point due to strong electrostatic forces.
5. These have low volatility due to strong electrostatic forces.
6. These are very hard. It is because, in these crystals ionic forces are present which are non-directional. As a result ions are attracted from all sides. Hence ions are closely packed and there is not much free space in these crystals.
7. The structure of an ionic crystal depends upon radius ratio. Ionic crystals having same radius ratio have same geometry.

   e.g. both NaCl and CsF have same radius ratio hence they have same geometry i.e. cubic.
8. Ionic crystals do not exist as individual, neutral, independent molecules. Therefore, term formula mass is used to express their mass instead of Molecular mass.
9. Ionic crystals do not conduct electricity in solid state. Because in solid form, ions have fixed position and therefore can not conduct electricity.

   However, these conduct electricity in molten state or in aqueous solution. Because in these forms, crystal lattice are broken up and ions become free. These free ions conduct electricity.
10. Ionic crystals are highly brittle.

   It is because, ionic crystal consists of parallel layers in which cations and anions are present in alternate positions. Thus, when a force is applied on the crystal, one layer of ions slides a little bit over the other layer. In this way like ions come in front of each other, which repel each other and thus a crystal is broken and show brittleness.

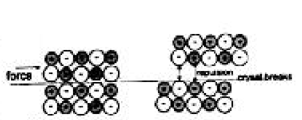
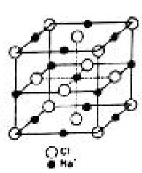


Figure: Explanation of high brittleness of ionic crystals

11. Due to close packing of ions in a crystal, these have high densities.
12. These are soluble in polar solvents like H_2O and produce ions
13. Since these crystals produce ions on dissolving in polar solvents. Thus their reactions in polar solvents are very fast.
14. They show isomorphism and polymorphism.

Structure of NaCl Crystal



- NaCl crystal is face-centred cubic and consists of Na^+ and Cl^- ions.
- Na^+ has 10 electrons, while Cl^- has 18 electrons. Thus Cl^- is larger in size than Na^+ ion.

- In NaCl crystal, each Na^+ ion is surrounded by six Cl^- ions, which are present at the corners of a regular octahedron. So the co-ordination number of Na^+ is six.
- Similarly each Cl^- ion is also surrounded by six Na^+ ions. Its co-ordination number is also six.

Calculation of number of Na^+ and Cl^- ions per unit cell.

Number of Cl^- ions

The figure shows that in NaCl cyrstal two types of Cl^- ions are present

(i) 8 Cl^- ions are present at the corners. Each of these is shared by 8 unit cells. Hence share of 1 unit cell $= \frac{8}{8} = 1$

(ii) 6 Cl^- ions are present at the faces. Each of these is shared by 2 unit cells. Hence share of 1 unit cell $= \frac{6}{2} = 3$

Hence one unit cell has $3 + 1 = 4$ Cl^- ions

Number of Na^+ ions

The figure shows that in NaCl cyrstal two types of Na^+ ions are present.

(i) 12 Na^+ ions are present along the edges, each of which is shared by four unit cells

Hence share of one unit cell $= \frac{12}{4} = 3$

(ii) 1 Na^+ ion is present at the centre, which is shared only by one unit cell.

Hence one unit cell has $3 + 1 = 4$ Na^+ ion.

Total number of Na^+ and Cl^- ions

One unit cell of NaCl has 4 Na^+ ions and 4 Cl^- ions.

Thus the ratio of Na^+ and Cl^- ions is 1 : 1.

Facts about NaCl:

- In NaCl, the distance between two similar ions is 5.63 A°.
- Thus the distance between two different ions is $\frac{5.63}{2} = 2.815$ A°.
- In NaCl crystal, no independent NaCl molecule is present. However, NaCl molecule exist in vapour phase.
- The radius ratio of NaCl is 0.53

Lattice Energy

The amount of energy released when one mole of the ionic crystal is formed from the gaseous ions is called lattice energy.

In this case the energy is given negative value.

OR

The energy required to break one mole of solid into isolated ions in the gas phase is called lattice energy.

In this case the energy is given positive value.

Lattice energy is measured in kJ mol^{-1}

Table: Lattice energies of ionic solids	
Ionic compound	Lattice Energy (kJ mol^{-1})
LiCl	-833
NaF	-895
NaCl	-787
KCl	-690
NaBr	-728
KBr	-665
NaI	-690

Examples:

$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$ $\Delta H = -787$ kJ $mole^{-1}$

$NaCl_{(s)} \rightarrow Na^+_{(g)} + Cl^-_{(g)}$ $\Delta H = +787$ kJ $mole^{-1}$

Lattice energy decreases with increase in size of cations or anions.

It is because due to increase in size, the packing of ions becomes less tight. Thus, more empty spaces are present and structure is loose. So, less amount of energy is required to break it. Hence, lattice energy of crystals decreases with increase in size of cations or anions.

Exercise Q.7 (b):

What are covalent solids? Give their properties. Explain the structure of diamond.

COVALENT SOLIDS

The crystalline solids in which neutral atoms are held together by covalent bonds are called covalent crystals

- These are also known as atomic solids.
- The atoms may be of same or different elements.

Covalent crystals are of two types

(i) **Giant Covalent Solids:** The crystal in which atoms are joined together to form big molecules.

Examples: Diamond, SiC or AlN etc.

(ii) **Layered Covalent Solids:** The crystal in which atoms are joined together to form separate layers.

Examples: graphite, cadmium iodide and BN etc.

Properties of Covalent Solids

1. These crystals have a three-dimensional network of atoms joined together by covalent bonds.
2. Since covalent bonds are directional bond, therefore, considerable free space is present in these crystals and their packing is looser than ionic crystals. Covalent crystals have open structure.
3. These are hard and a lot of energy is required to break them
4. These have high melting points and boiling points.
5. These have low volatility due to strong covalent bonds.
6. In these, no free ions are present, hence these are generally bad conductor of electricity.

   However, in graphite parallel layers have free electrons. Hence it is a good conductor of electricity parallel to its layer. However, graphite is not a conductor perpendicular to its layers.
7. These are insoluble in polar solvents like water but soluble in non-polar solvents like benzene, CCl_4 etc.

   Covalent crystals having big molecules like diamond, SiC etc are insoluble in all solvents. It is because they cannot develop forces with solvent molecules due to their big size.
8. These crystal show very slow reactions.

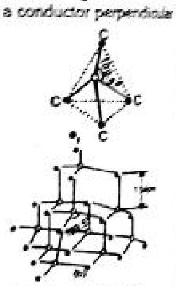


Figure: Structure of diamond crystal

Structure of Diamond

Diamond is an allotropic form of carbon.

There are four valence electrons in carbon.

The four orbitals (one 2s and three 2p) undergo sp^3 hybridization to give four sp^3 hybrid orbitals.

Thus, each carbon has four sp^3 hybrid orbitals, which are directed towards the corners of a regular tetrahedron. This is the unit cell of diamond. Many unit cells undergo $sp^3 - sp^3$ overlapping to form a huge three dimensional structure of diamond. sp^3-sp^3 overlapping form covalent bonds.

Figure: Face centred cube structure of diamond

Each carbon is linked to four other carbon atoms through covalent bonds. The structure of diamond is continuous and carbon-carbon overlapping form a big structure. The whole crystal looks like a huge carbon molecule. Thus, diamond is also called as the polymer of carbon.

In diamond all the bond angles are of 109.5° and the bond lengths are 154 pm. The overall structure of diamond is face centred cubic lattice.

Exercise Q.7 (c):

What are molecular crystals? Give their properties.

MOLECULAR SOLIDS

The crystalline solids in which polar or non-polar atoms or molecules of a substance form the crystal are called molecular crystals

e.g. In solidified noble gases, non-polar atoms are present.

Two types of intermolecular forces are present in molecular solids

a) Dipole-dipole interaction

b) van der Waal's forces

These forces are much weaker than ionic or covalent bonds

Examples:

Polar Molecular Crystals: Ice, Sugar

Non-Polar Molecular Crystals: iodine, sulphur, P, CO_2 etc

Properties of molecular Solids

1. These have regular arrangement of atoms in molecules. The position of atoms can be determined by X-rays analysis.
2. These are soft and easily compressible due to the presence of weak intermolecular forces.
3. These have low melting points and boiling points due to the presence of weak intermolecular forces.
4. These are mostly volatile due to the presence of weak intermolecular forces.
5. These are bad conductor of electricity, due to the absence of ions or free electrons.
6. These have large empty spaces, in a crystal hence these have low densities.
7. Sometimes, these are transparent to light.
8. Polar molecular crystals are soluble in polar solvents, while non-polar molecular crystals are soluble in non-polar solvents.
9. Generally, polar molecular solids have higher melting points and boiling points than non-polar molecular solids.

Figure: Structure of iodine molecules

Structure of I_2

In solid form, I_2 molecules have a layered structure.

In solid I_2, each I – I bond distance is 271.5 pm This distance is much longer than I – I distance in gaseous iodine, which is 266.6 pm. This structure shows that I_2 is a poor conductor of electricity

Exercise Q.8 (a):

Give different theories of a metallic bond. How does electron sea theory justifies the electrical conductivity, thermal conductivity and shining surface of metals?

METALLIC SOLIDS

The metal atoms in a metallic crystal are held together by special type of bonds called metallic bonds

Theories of Metallic Bonding

To explain metallic bonding, following theories have been proposed

1. Electron gas theory 2. Valence bond theory
3. Molecular orbital theory

1. Electron Gas Theory

It was proposed by Drude and improved by Loren (1923).

According to this theory, all the atoms of the metallic crystal loose their valence electrons. These electrons form an electron pool or electron gas in which positively charged nuclei are present at definite positions at a measurable distance.

The electrons of the sea are not attached to a particular nucleus. These electrons are delocalized over the entire crystals, therefore, these are called Free electrons.

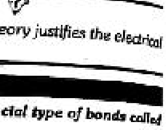


Figure: Positive ions surrounded by mobile electrons

The positively charged nuclei are held together by the free electrons throughout the lattice. The force, which binds a metal cation to a number of electrons around it, is called Metallic bond.

2. Valence Bond Theory

It was proposed by L. Pauling

According to this theory, metallic bonds are actually covalent bonds. However, these covalent bonds are highly delocalized and extended over whole crystal.

3. Molecular Orbital Theory (or Band Theory)

According to this theory, valence orbitals of metals overlap with each other to form delocalized orbitals. These are called molecular orbitals. Molecular orbitals are spread over the whole crystal. The electrons in filled orbitals are localized.

Actually, when large number of valence orbitals of atoms overlap, they produce large number of molecular orbitals. These molecular orbitals have very close energy states and thus form a band of energy states. Hence, this theory is also called Band theory.

The energy difference between two bands determines the properties of metallic crystals.

Properties of Metallic Solids

(Explanation of properties on the basis of Electron Gas Theory)

1. Electrical Conductivity

Metals are good conductor of electricity. When a metal is connected between two poles of battery, the mobile electrons begin to move towards positive pole and the electrons enter into the metal from negative pole. In this way metals conduct electricity as shown in the figure.

Figure: Explanation of electrical conductivity of a metal

Sometimes electrical conductivity decreases with increase in temperature.

It is because, increase in temperature, increases the vibrational motion of positive nuclei. These nuclei produce hindrance in the motion of free electrons.

Hence electrical conductivity decreases.

2. Thermal Conductivity

These are good conductor of heat.

During this free electrons take up heat from one end and transfer it throughout the crystal during their motion and collision with other electrons. Thus free electrons cause thermal conduction in metals.

3. Lustrous Surface

Metals have lustrous surface

The freshly cut surface of metals show shining (lustrous surface). It is because when a light strike the free electrons in the surface, they are excited. When these excited electrons come to their original position, they emit light. Thus light appears to be reflected by metal surface and it appears shining.

4. Malleable And Ductile

Metals are malleable and ductile.

When a force is applied on metals, their layer slip over each other and their shape is changed. Hence, these can be converted into sheets (malleable) or wires (ductile) without breaking.

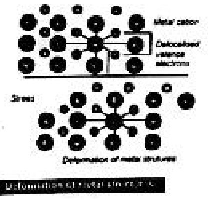


Figure: Deformation of metal structure

Exercise Q.8 (b):

Explain with the help of diagram (i)Cubic close packing in the structure of metals.
(ii) Hexagonal close packing in the structure of metals.

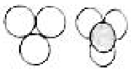
STRUCTURE OF METALS

In metals free electrons are present while positively charged nuclei acts as spheres. These spheres are closely packed together to form metallic crystals.

Close packing of spheres is done in following ways.

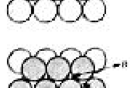
- Consider three balls joined in one plane as shown in fig. There is present a hole in between these balls. The hole is called interstices or crevices.

  If a fourth ball is placed on this hole, a tetrahedral structure is obtained as shown in the fig.



- Now consider the packing of eleven spheres as shown in fig. In this layer holes will be developed.
- Now a second layer of spheres is placed directly above the holes of first layer.

By this arrangement, all the holes of bottom layer are not covered by the spheres of top layer.



Hence, two types of holes will be produced.

(a) Holes created between spheres of second layer. Through this layer spheres of bottom layer can be seen. These are marked A.

(b) Holes which are not completely covered by top layer. Through this layer ground can be seen. These are marked B.

Now a third layer can be placed in two ways

(a) (Hexagonal Close-Packed Structure)

- If third layer is placed directly above the holes marked A, then the spheres of third layer will be directly above the spheres of first layer.
- This arrangement produces an ABAB or 1212 pattern
- This structure is called hexagonal close-packed structure.

(b) (Cubic Close-Packed Structure)

- If third layer is placed directly above the holes marked B, then the spheres of all the three layers will have different pattern.
- This arrangement produces an ABCABC or 123123 pattern.
- This structure is called face-centred cubic lattice.

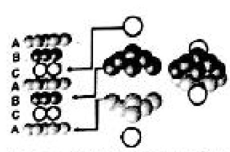


Figure: (a) Cubic close packing or Face centred cubic arrangement (ABCABC...)

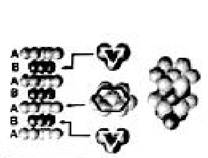


Figure: (b) Hexagonal close packing arrangement (ABAB...)

Table: Types of Solids

Type of Solid	Structural Particles	Intermolecular Forces	Typical Properties	Examples
Metallic	Cations plus delocalized electrons	Metallic bonds	Hardness varies from soft to very hard; melting point varies from low to very high; lustrous; ductile; malleable; very good conductors of heat and electricity	Na; Mg; Al; Fe; Zn; Cu; Ag; W
Ionic	Cations and anions	Electrostatic attraction	Hard; moderate to very high melting points; non-conductors of electricity (but good electrical conductors in the molten state)	NaCl; $NaNO_3$; MgO
Molecular	Molecules (atoms of noble gases)	London and / or dipole-dipole and / or hydrogen bonds	soft; low melting points; non-conductors of heat and electricity; sublime easily in many cases	Noble-gas elements; CH_4; CO_2; P_4; S_8; I_2; H_2O
Network covalent	Atoms	Covalent bonds	very hard; very high melting points; non-conductors of electricity	C(diamond); SiC; SiO_2

DETERMINATION OF AVOGADRO'S NUMBER (N_A)

Many methods are used for the calculation of Avogadro's Number.

An accurate method is based on the study of crystals.

To determine N_A by crystallographic method following data is required

- The volume of one mole of a crystalline solid.

  It can be determined from its density
- The distance between particles in the crystal lattice.

  It can be determined by X-rays

Example:

Consider LiF crystal. It has a cubic crystal. It density is 2.65 g cm^{-3}.

Calculations

(i) The distance between Li^+ and F^- ions is 2.01 A° = 2.01×10^{-8} cm

(ii) Formula mass of LiF = M = 6.939+18.9984 = 25.9374 g mol^{-1}

Density = d = 2.65 g cm^{-3}

Molar Volume = V = ?

Since

$$d = \frac{M}{V}$$

$$\text{or} \quad V = \frac{M}{d} = \frac{25.9374}{2.65} = 9.788 \text{ cm}^3$$

(iii) This volume can be used to find the edge length of the cube.

Since all the lengths in a cube are equal, therefore, we can write

$$\ell \times \ell \times \ell = V$$

$$\ell^3 = V$$

$$\text{or Edge length} = \ell = \sqrt[3]{V}$$

$$= \sqrt[3]{9.788}$$

$$= 2.139 \text{ cm}$$

(iv) The number of ions along one edge length $= \dfrac{\text{lenght of edge}}{\text{distance between ions}}$

$$= \frac{2.139 \text{ cm}}{2.01 \times 10^{-8} \text{ cm ion}^{-1}}$$

$$= 1.064 \times 10^{8} \text{ ions}$$

(v) Thus the total number of ions in the cube $= (1.064 \times 10^{8})^3$

$$= 1.204 \times 10^{24} \text{ ions}$$

(vi) In a cube, total no. of ions include, one Avogadro's No of Li^+ ions and one Avogadro's number of F^- ions.

$$\text{Therefore Avogadro's No} = \frac{1.204 \times 10^{24}}{2} = 6.02 \times 10^{23}$$

OBJECTIVE AND SHORT ANSWER QUESTIONS (EXERCISE)

Q1. Multiple-choice questions

(i) Ionic solids are characterized by *(Gujranwala board, 2012)*

(a) Low melting point
(b) Good conductivity in solid state
(c) High vapour pressure
(d) Solubility in polar solvents

(ii) Amorphous solids

(a) Have sharp melting point
(b) Undergo clean cleavage when cut with knife
(c) Have perfect arrangement of atoms.
(d) Can possesses small regions of orderly arrangement of atoms

(iii) The molecules of CO_2 in dry ice form the

(a) Ionic crystals (b) covalent crystals
(b) molecular crystals (d) any type of crystal

(D.G Khan Board, 2009) (Rawalpindi Board, 2010, 2012) (D.G. Khan Board' 2012) (Lahore board, 2013) (Sargodha Board, 2014)

(iv) Which of the following is a pseudo solid

(a) CaF_2 (b) Glass (c) NaCl (d) All

(Faisalabad Board, 2009) (Bahawalpur Board, 2009) (Rawalpindi Board, 2009) (Multan Board, 2010, 2011, 2012) (Gujranwala board, 2014)

(v) Diamond is a bad conductor because *(Gujranwala board, 2013)*

(a) It has tight structure
(b) It has high density
(c) There is no free electron present in the crystal of diamond to conduct electricity
(d) None of the above

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (d)
In ionic solids oppositely charged ions are held together by strong electrostatic forces. Therefore, ionic solids are polar compounds. Hence, according to solubility principle, "Like dissolve Like", ionic solids are dissolved in polar solvents.

(ii) Ans: (d)
Amorphous solids have random arrangement of particles. However, these solids have areas of short-range order in their structure. These areas are called crystalites.

(iii) Ans: (c)
In dry ice, molecules of CO_2 are held together by weak intermolecular forces. Hence, it will form molecular crystals.

(iv) Ans: (b)
NaCl and CaF_2 are ionic crystalline solids. While glass is an amorphous solid. Amorphous solids are also known as pseudo solids.

(v) Ans: (c)
In diamond, each carbon is linked to four other carbon atoms through covalent bonds. Thus, valency of carbon is fully satisfied and no free electrons are present in diamond. Hence, diamond is a bad conductor of electricity.

Q.2 Fill in the blanks

(i) In a crystal lattice, the number of nearest neighbours to each atom is called the ______.

(ii) There are ______ Bravis lattices.

(iii) Pseudo solids are regarded as ______ liquids.

(iv) Glass may begin to crystallize by a process called ______.

(v) Substance, which exhibits the same ______ in all directions, are called ______.

(vi) The branch of science, which deals with the ______ of crystals is called crystallography.

Answers:
i) Co-ordination number ii) Fourteen iii) super-cooled iv) annealing
v) physical properties, isotrope vi) geometry and structure

Q.3 Indicate True or False

(i) There are five parameters in unit cell dimensions of a crystal.

(ii) Ionic crystals are very hard, have low volatility and very low melting point and boiling points.

(iii) The value of lattice energy of the ionic substances depends upon the size of ions.

(iv) Molecular orbital theory of solids is also called band theory

(v) Ionic solid is good conductor of electricity in the molten state

Answers:
(i) False (ii) False (iii) True (iv) True (v) True

Q.4 ***What are solids? Give general properties of solids. How do you differentiate between crystalline solids and amorphous solids.***

Solved on page 202

Q.5 (a) *Explain the following properties of crystalline solids. Give three examples in each case.*

(i) Anisotropy	***(ii) Cleavage***
(iii) Habit of a crystal	***(iv) Isomorphism***
(v) Transition temperature	***(vi) Symmetry***
(vi) Growing of a crystal	***(vii) Polymorphism***

Solved on page 206

(b) How polymorphism and allotropy are related to each other? Give examples.

Polymorphism

- ***The phenomenon in which a substance exists in more than one crystalline form is called polymorphism.***
- This term is used for compounds
- Polymorphs of a substance have same chemical properties but different physical properties.

Examples:

$AgNO_3$ exists as Rhombohedral, Orthorhombic

$CaCO_3$ exists aa Trigonal and orthorhombic

Allotropy

The phenomenon in which an element exists in more than one crystalline form is called allotropy.

- This term is used for elements
- Allotropes of a substance have same chemical properties but different physical properties.

Examples:

- Carbon can exist in graphite (Hexagonal) and diamond (cubic) forms.
- Sulphur can exist in Rhombic and Monoclinic forms.

Q.6 (a) ***Define unit cell. What are unit cell dimensions? How the idea of crystal lattice is developed from the concept of unit cell?***

Solved on page 203

(b) Explain seven crystal systems and draw the shapes of their unit cells.

Solved on page 204

Q.7 (a) ***What are ionic solids? Give their properties. Explain the structure of NaCl. Sketch a model to justify that unit cell of NaCl has four formula units in it.***

Solved on page 210

(b) What are covalent solids? Give their properties. Explain the structure of diamond.

Solved on page 213

(c) What are molecular crystals? Give their properties.

Solved on page 215

(d) Justify that molecular crystals are softer than ionic crystals.

(D.G. Khan Board, 2009)

Ionic solids are very hard. It is because these crystals have non-directional ionic bonds. As a result, ions are attracted from all sides. Hence ions are closely packed and there is no much free space in these crystals. Therefore, these are hard.

But molecular solids have very weak intermolecular forces. Thus these are soft and easily compressible.

Q.8 (a) Give different theories of a metallic bond. How does electron sea theory justifies the electrical conductivity, thermal conductivity and shining surface of metals?

Solved on page 216

(b) Explain with the help of diagram

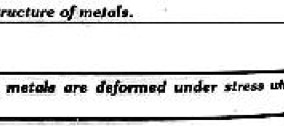
(I) Cubic close packing in the structure of metals.

(II) Hexagonal close packing in the structure of metals.

Solved on page 218

Q.9 Crystals of salts fracture easily, but metals are deformed under stress without fracturing. Explain the difference.

Salts are ionic and ionic crystals are highly brittle and can fracture easily.



It is because, ionic crystals consist of parallel layers in which cations and anions are present in alternate positions. Thus, when a force is applied on the crystal, one layer of ions slides a little bit over the other layer. In this way like ions come in front of each other, which repel each other and thus crystal is broken.

However, metals do not consist of oppositely charged ions. Thus, when a force is applied on metals, their layers just slip over each other. There is no repulsion between the layers. Hence, these can be converted into sheets (malleable) or wires (ductile) without breaking.

Q.10 What is the coordination number of an ion? What is the coordination number of the cation in (a) the NaCl structure and (b) the CsCl structure? Explain the reason for this difference?

The number of nearest neighbours of an ion in an ionic crystal is called co-ordination number of ion.

e.g. In NaCl crystal, each Na^+ ion is surrounded by six Cl^- ions, which are present at the corners of a regular octahedron. So the co-ordination no. of Na^+ is six.

Similarly each Cl^- ion is also surrounded by six Na^+ ions. Its co-ordination no. is also six.

a) In NaCl, the co-ordination no. of cation i.e. Na^+ is 6.

b) In CsCl, the co-ordination no. of cation i.e. Cs^+ is 8.

For this difference see (Q.12 , part xv)

Q.11 Give examples of ionic solids, molecular solids and covalent macromolecular solids. What are the factors which determine whether each of these types of solid will dissolve in water or not?

The general solubility principle is ***"Like Dissolve Like"***. Thus, polar substances dissolve in polar solvents and non-polar substances dissolves in non-polar solvents. Water is a polar solvent. Following factors affect the solubility of substances in water.

(i) Polarity: Polar substances dissolve in water easily.

(ii) Lattice Energy: Higher is the lattice energy, difficult is the crystal lattice to break, therefore, lesser is the solubility.

(iii) Size of ions/molecules: The solubility of a substance in water decreases with increase in size of ions/molecules.

Ionic Solids:

Examples: NaCl, $BaCl_2$, K_2SO_4 etc.

These are polar therefore; generally soluble in water. However, ionic solids with high lattice energy or large size ions are less soluble. e.g., NaF (High lattice energy) and $BaCO_3$ (Large size ions)

Molecular Solids:

Examples:

Polar molecular solids: Ice, Sugar

Non-Polar molecular solids: Iodine, sulphur, P , CO_2 etc

Polar molecular solids are generally soluble in water, while non-polar molecular solids are soluble in non-polar solvents.

Covalent Macromolecular Solids:

Examples: Diamond, SiC etc.

Covalent solids are non-polar so these are generally insoluble in polar solvents like water but soluble in non-polar solvents like benzene, CCl_4 etc. However, covalent macromolecular solids like diamond, SiC etc are insoluble in all solvents. It is because they cannot develop forces with solvent molecules due to their big size.

Q.12 Explain the following with reasons:

(i) Sodium is softer than copper but both are very good electrical conductors.

(Gujranwala Board, 2008; Sargodha Board, 2014)

The forces in metallic solids depend upon number of valence electrons. Greater the number of valence electrons, stronger the forces. Sodium has lesser number of electrons in its valence shell, therefore, it has weak forces. Copper has more number of valence electrons, therefore, it has stronger forces. Thus, due to weaker forces, sodium is softer than copper.

However, both are metals and have free electrons. Hence, both are good conductors of electricity. However, due to more free electrons in Cu, it is a better conductor than Na.

(ii) Diamond is hard but an electrical insulator

(D.G. Khan Board, 2007; Gujranwala Board, 2011, 2013; Lahore Board, 2008, 2013; Bahawalpur Board, 2009; Sargodha Board, 2014)

In diamond, each carbon is sp^3 hybridized. Each carbon is linked to four other carbon atoms through covalent bonds. Due to strong bonding in diamond, it is hard.

However, in diamond crystal free electrons are not present. Therefore, it cannot conduct electricity. Hence, it is an electrical insulator.

(iii) Sodium chloride and Caesium chloride have different structures.

(Azad Kashmir Board, 2012)

NaCl and CsCl have different structure. It is because Na^+ ion is smaller than Cs^+ ion. Thus, Na^+ is surrounded by only 6 Cl^- ions in NaCl crystal and its co-ordination no. is only 6. While due to larger size of Cs^+ ions, it is surrounded by 8 Cl^- ions. Thus, its co-ordination number is 8.

Moreover, due to different sizes of Na^+ and Cs^+ ions, both NaCl and CsCl have different radius ratio.

Hence, both NaCl and CsCl have different structures. NaCl have face-centred cubic lattice and CsCl have body centred cubic lattice.

(iv) Iodine dissolves readily in tetra chloromethane.

(Lahore Board, 2014)

Generally, polar substances dissolve in polar solvents, while non-polar dissolves in non-polar solvents.

Since I_2 is non-polar and tetrachloromethane (CCl_4) is also non-polar. Hence, I_2 dissolve in CCl_4

(v) The vapour pressure of the solids is far less than those of liquids.

(Faisalabad Board, 2005)

In solids, intermolecular forces are much stronger than liquids. Thus, it is very difficult to vaporize solids. Hence, solids have low vapour pressure than liquids.

(vi) Amorphous solids like glass is also called super cooled liquid.

True solids have ordered arrangement of particles, while liquids have somewhat random structure.

Amorphous solids also have random arrangement of particles. Thus, their molecular structure is more like liquids. Hence, amorphous solids are called as super cooled liquid.

e.g. glass, rubber etc.

(vii) Cleavage of the crystals is itself anisotropic behaviour.

(D.G. Khan Board, 2010; D.G. Khan Board, 2010; Bahawalpur Board, 2011; Gujranwala Board, 2012; Lahore Board, 2014)

Each crystal has definite arrangement of particles. Therefore a crystal can be broken easily in a particular plane only and not in any other plane.

Thus, cleavage depends upon the direction of plane. The properties, which depend upon direction, are called anisotropic properties. Hence, cleavage is an anisotropic behaviour.

e.g. Mica crystal consists of a large number of parallel sheets. These sheets can be easily separated only parallel to their lengths.

(viii) The crystals showing isomorphism mostly have the same atomic ratios.

(Lahore Board, 2008)

A crystalline form does not depend upon the chemical nature of atoms. It only depends upon, no of atoms, sizes of atoms and way of combination of atoms.

Hence, substances with same no. of atoms i.e. same atomic ratio, generally, have same crystal structure and hence they are isomorphous.

(ix) The transition temperature is given by elements having allotropic forms and compounds showing polymorphism.

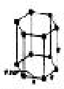
Different allotropic forms of elements and polymorphous forms of a compound can be converted into each other by controlling temperature.

The temperature at which transition of one crystalline form to other crystalline form takes place is called transition temperature.

Thus, concept of transition temperature cannot be used for substances, which have only one form.

Hence, transition temperature is only given by elements showing allotropy and by compounds showing polymorphism.

(x) One of the unit cell angles of Hexagonal crystal is 120°



In hexagonal crystal, one of the angles is of 120°. It is present inside the hexagon as shown in the fig.

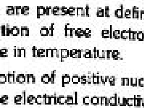
(xi) The electrical conductivity of the metals decreases by increasing temperature.

(Sargodha Board, **2010, 2013**: Gujranwala Board, **2014**)

A metal consists of sea of free electrons in which positive nuclei are present at definite positions. The electrical conductivity of metals is due to the motion of free electrons. Sometimes the electrical conductivity of metals decreases with increase in temperature.

It is because, increase in temperature increases the vibrational motion of positive nuclei. These nuclei produce hindrance in the motion of free electrons. Hence electrical conductivity decreases.

(xii) In the closest packing of atoms of metals, only 74% space is occupied.



In close-packed structure, layers of metal atoms in the form of spheres are present over each other. In this arrangement, spaces are left behind in the layers as shown in the fig. These spaces are called interstices or crevices. Due to these spaces, volume occupied by atoms of metal is less than the total available volume. Thus it has been found that in close-packed structure of metals, 74% of the total volume is occupied. The unutilized 26% space consists of interstices.

(xiii) Ionic crystals don't conduct electricity in the solid state. OR Ionic solids are insulators in solid state but become conductor when dissolved in water. Explain.

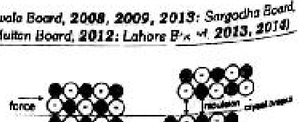
(Bahawalpur Board **2012**: Lahore Board, **2008, 2013, 2014**: Multan Board, **2010, 2011, 2013**: D.G. Khan Board, **2012**: Azad Kashmir Board, **2012**: Faisalabad Board, **2013**)

Ionic crystals do not conduct electricity in solid state. It is because, in solid form, ions have fixed position and therefore they cannot conduct electricity.

However, these conduct electricity in molten state or in aqueous solution. Because in these forms, crystal lattice are broken up and ions become free. These free ions can conduct electricity.

(xiv) Ionic crystals are highly brittle.

(Faisalabad Board, **2007**: D.G. Khan Board, **2008**: Gujranwala Board, **2008, 2009, 2013**: Sargodha Board, **2009**: Sargodha Board, **2010**: Bahawalpur Board, **2011**: Multan Board, **2012**: Lahore Board, **2013, 2014**)



It is because, ionic crystals consist of parallel layers in which cations and anions are present in alternate positions.

Thus when a force is applied on the crystal, one layer of ions slides a little bit over the other

layer, in this way like ions come in front of each other, which repel each other and thus a crystal is broken and show brittleness.

(xv) The number of positive ions surrounding the negative ion in the ionic crystal lattice depends upon the sizes of the two ions.

The no. of ions surrounded by a particular ion (i.e. co-ordination no.) depends upon the relative sizes of two ions.

e.g. If a small negative ion gets surrounded by a large positive ion, the co-ordination no. will be small and vice versa.

The relative sizes of ions are indicated by radius ratio. Generally, greater the radius ratio, greater is the co-ordination no. and vice versa.

e.g. Consider the case of NaCl and CsCl

NaCl has small Na^+ ion and less radius ratio than CsCl i.e. 0.53.

Therefore its co-ordination no. is 6.

CsCl has larger Cs^+ ion and larger radius ratio of 0.93 than NaCl.

Therefore, its co-ordination no. is 8.

IMPORTANT DEFINITIONS

Radius Ratio

It is the ratio of the radius of cation to anion in an ionic crystal.

i.e. radius ratio = $\frac{\text{radius of cation}}{\text{radius of anion}}$

It is used to express the relative sizes of different ions

Example

The radius ratio of NaCl is 0.53

The radius ratio of CsCl is 0.93

Co-Ordination Number

The number of nearest neighbours of a particle in a crystal is called its co-ordination number.

e.g. In NaCl crystal, each Na^+ ion is surrounded by six Cl^- ions, which are present at the corners of a regular octahedron. So the co-ordination no. of Na^+ is six.

Similarly, each Cl^- ion is also surrounded by six Na^+ ions. Its co-ordination no. is also six.

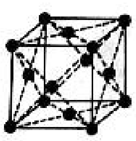
Co-ordination number depends upon radius ratio

Generally, greater the radius ratio, greater is the co-ordination no. and vice versa.

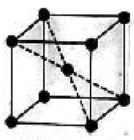
e.g.

Radius ratio	Co-ordination No.
Above 0.73	8
0.414 – 0.73	6
0.225 – 0.414	4
0.155 – 0.225	2

SOME CRYSTALLINE FORMS



Face-centered
CUBIC



Body-centered
CUBIC

HELLO! Mr. Question here!

Multiple Choice Questions from PAST PAPERS

1. Allotropy is the property of? *(D.G. Khan Board, 2010: Gujranwala board, 2011: Sargodha Board, 2013)*
   (a) compound (b) element (c) atom (d) mixture
2. Dry Ice (Solid CO_2) is an example of solid: *(Lahore board, 2014)*
   (a) Covalent (b) Molecular (c) Ionic (d) Metallic
3. The crystals formed due to London forces interaction are: *(Gujranwala board, 2008, 2010)*
   (a) ionic (b) covalent (c) molecular (d) metallic
4. How many allotropic forms are present in carbon: *(Gujranwala board, 2009)*
   (a) two (b) three (c) four (d) five
5. Diamond and graphite are examples of: *(Multan Board, 2011)*
   (a) Isomorphism (b) Polymorphism (c) Isomerism (d) Allotropy
6. When a = b ≠ c and $\alpha = \beta = 90^\circ = \gamma = 120^\circ$ *(Rawalpindi Board, 2013)*
   (a) Cubic (b) Triclinic (c) Hexagonal (d) Monoclinic
7. The Carbon atom in diamond is: *(Multan Board, 2013)*
   (a) sp^3 hybridized (b) sp hybridized (c) sp2 hybridized (d) dsp^2 hybridized
8. Transition temperature of tin is: *(Lahore Board, 2009)*
   (a) 95.5°C (b) 13.2°C (c) 0°C (d) 128.5°C
9. The crystal of diamond is: *(Lahore Board, 2009)*
   (a) Ionic (b) Covalent (c) Molecular (d) Metallic
10. Structure of CrO_4^{2-} is *(Lahore Board, 2010)*
    (a) tetrahedral (b) octahedral (c) cubic (d) Triclinic
11. K_2SO_4 and K_2CrO_4 are isomorphous solids and exist in *(Sargodha Board, 2010)*
    (a) cubic form (b) orthorhombic form (c) Trignonal form (d) Tetragonal
12. The transition temperature of KNO_3 is *(Sargodha Board, 2010)*
    (a) 13.2°C (b) 95.5°C (c) 128°C (d) 32.02°C
13. Crystal system shown by diamond is: *(Bahawalpur Board, 2010)*
    (a) cubic (b) tetragonal (c) Monoclinic (d) Hexagonal
14. Amorphous solids *(D.G. Khan Board, 2012)*
    (a) have sharp melting point (b) undergo cleavage when cut with knife
    (c) have perfect arrangement of atoms
    (d) can possesses small regions of orderly arrangement of atoms

15. A crystal system in which all the axes and angles are unequal is called: **(Lahore Board, 2007)**
    (a) Tetragonal system (b) monoclinic system
    (c) triclinic system (d) cubic system
16. LiF is a crystalline substance and has **(Rawalpindi Board, 2010)**
    (a) ionic crystals (b) metallic crystals (c) covalent crystals (d) molecular crystals
17. Which of the following is a pseudo solid? **(Sargodha Board, 2011)**
    (a) CaF_2 (b) NaCl (c) glass (d) MgO
18. Crystal of diamond is? **(Sargodha Board, 2011)**
    (a) ionic (b) covalent (c) molecular (d) metallic
19. Which of the following is a pseudo solid? **(Sargodha Board, 2012)**
    (a) CaF_2 (b) glass (c) NaCl (d) KBr
20. Which one is not an isomorphs pair? **(Faisalabad Board, 2010)**
    (a) $NaNO_3$, $CaCO_3$ (b) NaF, MgO (c) K_2SO_4, $K_2Cr_2O_7$ (d) Zn, Cd
21. The example of hexagonal system is **(Lahore Board, 2011)**
    (a) Sulphur (b) NaCl (c) Graphite (d) Diamond
22. Transition temperature of Tin (Sn) is: **(Faisalabad Board, 2011)**
    (a) 128°C (b) 95.5°C (c) 13.2°C (d) 32.8°C

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(b)	2	(b)	3	(c)	4	(a)	5	(d)
6	(c)	7	(a)	8	(b)	9	(b)	10	(a)
11	(b)	12	(c)	13	(a)	14	(d)	15	(c)
16	(a)	17	(c)	18	(b)	19	(b)	20	(c)
21	(c)	22	(c)						

SHORT & LONG QUESTIONS FROM PAST PAPERS

AMORPHOUS SOLIDS, CRYSTALLINE SOLIDS, UNIT CELL

Short Questions

(1) Define amorphous solid. Give example. **(D.G. Khan Board, 2008)**
(2) Differentiate between amorphous solids and crystalline solids. **(Sargodha Board, 2011)**
(3) Define crystal and crystallite. **(Bahawalpur Board, 2009)**
(4) Define crystal lattice with an example. **(Bahawalpur Board, 2009)**

(5) What is a unit cell? **(Multan Board, 2008)** OR Draw the shape of a unit cell mentioning angles and axes. **(D.G. Khan Board, 2010)** OR Describe (or What are) crystallographic elements. **(Faisalabad Board, 2011: Gujranwala Board, 2014)**

Long Questions

(1) Define Unit cell. Draw diagram and give dimensions of hexagonal system of crystals. **(Multan Board, 2009)**

PROPERTIES OF CRYSTALLINE SOLIDS

Short Questions

(1) Explain cleavage of the crystals and cleavage plane. **(Rawalpindi Board, 2011, 2012)**
(2) Define (a) cleavage plane (b) unit cell. **(Faisalabad Board, 2010)**
(3) Graphite is conductor but diamond is insulator. Give reason. **(Faisalabad Board, 2011)**
(4) OR Why graphite is a good conductor of electricity? **(Sargodha Board, 2013)** OR Why graphite is anisotropic in electrical conductivity? **(Rawalpindi Board, 2007)**
(5) Differentiate between isotropy and anisotropy. **(Multan Board, 2011)**
(6) Why do you mean by symmetry? Give elements of symmetry? **(Sargodha Board, 2009)** OR Define symmetry. Name any two symmetry elements. **(Multan Board, 2007)**
(7) Write a brief note on (i) Anisotropy (ii) Isomorphism. **(Faisalabad Board, 2010)**
(8) Define the following terms with example. (i) Isomorphism (ii) Polymorphism (iii) Allotropy (iv) transition temperature **(D.G. Khan Board 2012)**
(9) Define the following terms with example. (i) Polymorphism (ii) Anisotropy (iii) Symmetry **(Gujranwala Board, 2008)**
(10) What is habit of a crystal? **(Gujranwala Board, 2009)**
(11) Define isomorphism with two examples. **(Rawalpindi Board, 2007: Lahore Board, 2007, 2011)**
(12) Define polymorphism with an example. **(Multan Board, 2008)**
(13) Define isomorphism and polymorphism with examples **(Faisalabad Board, 2007: Gujranwala Board, 2009: Lahore Board, 2013: Multan Board, 2013) Ans: Combine S2 and S3**
(14) Differentiate between isomorphism and polymorphism **(Multan Board, 2012: Sargodha Board, 2013)**
(15) Define allotropy. Give two allotropic forms of carbon. **(Bahawalpur Board, 2010)**
(16) Differentiate between polymorphism and allotropy. **(Rawalpindi Board, 2013)**
(17) Define transition temperature with two examples. **(Rawalpindi Board, 2011: Faisalabad Board, 2010; D.G. Khan Board, 2012: Multan Board, 2011: Lahore Board, 2010, 2014)**

IONIC SOLIDS, LATTICE ENERGY

Short Questions

(1) Why the ionic crystalline solids have high melting points? **(Faisalabad Board, 2008)** OR How the ionic crystalline solids have high melting points. **(D.G. Khan Board, 2009)**
(2) Define Lattice energy. Give example **(Lahore Board, 2008: Multan Board, 2012: Sargodha Board, 2012, 2013)**
(3) What is Lattice and Lattice energy? **(Rawalpindi Board, 2012)**
(4) Why ionic compounds do not show the phenomenon of isomerism? **(Lahore Board, 2010)**
(5) What is dry ice? Mention the type of solid to which it belongs? **(Bahawalpur Board, 2010)**
(6) NaCl is an insulator but Sodium is Conductor of electrons. Explain with reason. **(Sargodha Board, 2011)** OR Sodium is a good conductor of electricity but $NaCl_{(s)}$ is not. **(Lahore Board, 2011)**

Long Questions

(1) Define ionic solids. Discuss properties of ionic solids in detail. **(Sargodha board 2007: D.G. Khan board, 2007, 2011: Multan Board, 2010: Lahore Board, 2013)**

(2) Classify solids on the basis of bonding. How ionic solids are formed? Give two properties of ionic solids. **(Lahore Board, 2012)**

COVALENT SOLIDS

Short Questions

(1) Write two properties of covalent crystals. **(Gujranwala Board, 2011)**

Long Questions

(1) Briefly explain covalent solids, write their four uses. **(Sargodha Board, 2010)**

(2) What are covalent solids? Discuss the structure of Diamond. **(D.G. Khan Board 2010)**

[redacted] What are covalent crystals? Give their two types. Write properties of covalent crystals. **(Bahawalpur Board, 2011, 2012)**

(4) Molecular solids are soft and easily compressible. Why? **(Bahawalpur Board, 2008: Multan Board, 2010)**

MOLECULAR SOLIDS

Long Questions

(1) What are molecular solids. Give three properties of molecular solids. **(Lahore Board, 2009)**

(2) What are molecular solids? Give their three properties. **(Rawalpindi Board, 2010)**

(3) What are molecular solids? Give examples and explain their properties. **(Gujranwala Board, 2014: Lahore Board, 2014)**

METALLIC SOLIDS

Short Questions

(1) Explain electron gas theory. **(Lahore Board, 2010)** State electron pool theory. **(Multan Board 2011)**

(2) Metallic crystals are good conductor of electricity. Explain. **(Multan Board, 2007, 2009)** OR Why metals behave as good conductors of electricity? **(Rawalpindi Board, 2013)**

(3) A fresh cut metal has a shiny look. Justify. **(D.G. Khan Board, 2008)** OR Metallic crystals are lustrous in nature. Why? **(Sargodha Board, 2013)**

(4) Metals are malleable and ductile. Justify. **(Sargodha Board, 2007: D.G. Khan Board, 2011: Faisalabad Board, 2012)**

Long Questions

(1) Discuss the electron gas theory to explain the properties of metallic solids. **(Rawalpindi board 2007: Multan board, 2007)**

(2) What is electron pool theory regarding to metallic solids? Also give its four properties. **(Faisalabad Board, 2013)**

(3) Explain the electron gas theory of metals and discuss conductivity of metals. **(Multan Board, 2011)**

STRUCTURE OF METALS

Long Questions: (L1 means Long Question 1, etc.)

(1) Explain with the help of diagram.

(i) Cubic close packing in the structure of metals.

(ii) Hexagonal close packing in the structure of metals. **(Bahawalpur Board, 2010)**

TEST YOUR SKILLS — Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) Which type of forces are present among molecules of acetone?
(a) H-bond (b) London forces $\boxed{\text{(c) Dipole-dipole forces}}$ (d) Debye forces

(ii) I_2 has highest boiling point among its family members due to
(a) smaller size $\boxed{\text{(b) high polarizability}}$ (c) non-polar nature (d) all

(iii) Which of the following compound has H-bonding among its molecules?
$\boxed{\text{(a) } C_2H_5OH}$ (b) CCl_4 (c) I_2 (d) NaCl

(iv) Liquid crystals are
(a) anisotropic $\boxed{\text{(b) isotropic}}$ (c) solids (e) none

(v) Crystal of diamond is
(a) Ionic $\boxed{\text{(b) covalent}}$ (c) Molecular (d) metallic

(vi) How many Cl^- ions are there around Na^+ ion in NaCl crystal?
(a) 3 (b) 4 $\boxed{\text{(c) 6}}$ (d) 8

(vii) Crystals of covalent compounds always have
$\boxed{\text{(a) atoms as their structural units}}$ (b) atoms or molecules as their structural units
(c) high melting points (d) ions held together by electrostatic forces

(viii) An example of ionic crystal is
(a) diamond (b) quartz (c) solid CO_2 $\boxed{\text{(d) NaCl}}$

(ix) The solid NaCl is a bad conductor of electricity since
(a) in solid NaCl, there are no ions $\boxed{\text{(b) in solid NaCl there is no velocity of ions}}$
(c) solid NaCl is covalent (d) in solid NaCl, there are no electrons

(x) The transition temperature of KNO_3 is
(a) 13.2 °C (b) 95.5 °C $\boxed{\text{(c) 128°C}}$ (d) 32.02°C

(xi) Vapour pressure of a liquid depends upon:
(a) amount of liquid (b) surface area $\boxed{\text{(c) temperature}}$ (d) size of container

(xii) In DNA molecule, the hydrogen bonding is between
(a) C and H atoms $\boxed{\text{(b) N and H atoms}}$ (c) O and H atoms (d) O and N atoms

(xiii) Dipole dipole forces are present among
(a) Molecules of solid iodine (b) Atoms of neon gaseous state
$\boxed{\text{(c) chloroform molecules}}$ (d) carbon tetrachloride molecules

(xiv) It is very much difficult to cook food at Mount Everest, because
(a) Temperature of atmosphere is very low $\boxed{\text{(b) the boiling point of water is 69°C}}$
(c) water becomes heavier (d) the boiling point of water is increased

(xv) K_2SO_4 and K_2CrO_4 are isomorphous solids and exist in
(a) Cubic form $\boxed{\text{(b) Orthorhombic form}}$ (c) Trigonal form (d) Tetragomal

(xvi) Crystals formed due to London forces of interaction are
(a) Ionic (b) covalent $\boxed{\text{(c) molecular}}$ (d) metallic

(xvii) Which statement about isomorphic substances is incorrect
(a) They have different chemical properties $\boxed{\text{(b) They have same physical properties}}$
(c) They have same atomic ratio (d) They have definite geometric shape

SUBJECTIVE

Time: 2:10 Hours **Marks: 68**

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question numbers carefully. **(22x 2)=44**

Section – I

Q2. Answer any Eight parts from the followings.

(i) Why liquid crystals are so sensitive towards temperature, pressure electric signals and magnetic field?.

(ii) Physical state of halogens changes does the group. Why?
(iii) H_2O has higher boiling point than HF & NH_3. Why?
(iv) I_2 has higher heat of sublimation. Why?
(v) Water boils at low temperature on Murree Hills. Why?
(vi) Differentiate b/w Amorphous & crystalline solids.
(vii) Ionic crystals are brittle. Why?
(viii) Lattice energy increases with decrease in size of cation or anion. Why?
(ix) Covalent crystals are dissolved in non-polar solvents. Why?
(x) Define crystal lattice and lattice point.
(xi) Metallic crystals are not brittle. Why?
(xii) Bubbles continuously come out of a boiling liquid. Why?

Q3. Answer any Eight parts from the followings.
(i) What type of forces are present in substances like He, Ne, Ar, Cl_2, CH_4, etc.?
(ii) How sea life survives under frozen sea?
(iii) Boiling points of noble gasses increase down the group. Why?
(iv) Boiling point of C_2H_6 (ethane) is -88.6°C and that of C_6H_{14} is + 68.7°C. Why?
(v) HF is a weaker acid than HCl. Why?
(vi) Why H_2O is a liquid and H_2S is a gas at room temeperature?
(vii) Electronegativity of F is more than oxygen, but boiling point of water is higher than that of HF. Why?
(viii) Ethyl alcohol is soluble in water, but hydrocarbons are insoluble in water. Why?
(ix) Why the metals are malleable and ductile?
(x) Why acetone is soluble in chloroform?
(xi) Why the melting and boiling point of alkanes increase with increase in molar mass?
(xii) What is transition temperature?

Q4. Answer any Eight parts from the followings.
(i) Metallic crystals are lustrous. Why?
(ii) NaCl is an insulator but sodium is conductor of electrons. Explain with reason?
(iii) Ice floats on water. Justify it
(iv) Why cleavege is an anisotropic behaviour?
(v) Define crystal lattice and lattice point?
(vi) What is the relationship between boiling point of a liquid and external pressure?
(vii) What do you mean by symmetry? Give elements of symmetry?
(viii) Ionic compounds do not have molecule. Why?
(ix) Molecular crystals are soft. Why?

Section – II (Attempt any three questions) (8x 3)=24

Q5. (a) What are covalent solids? Gove their properties. (03)
(b) Give five uses of liquid crystals. (03)
(c) Differentiate b/w isomorphism & polymorphism. (02)

Q6. (a) What is polarizability? On What factors does it depend? (02)
(b) What is the mechanism of generation of London forces? (03)
(c) How does H-bonding saves the aquatic life? (03)

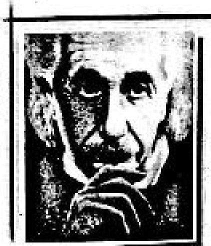
Q7. (a) Define Allotropy. Give examples. (02)
(b) Define crystal system. Describe tetragonal, hexagonal and orthorhombic crystal systems. (04)
(c) Ionic crystals do not conduct electricity in solid form. Why? (02)

Q8. (a) How does crystallography helps to determine Avogadro's number? (04)
(b) Evaporation causes cooling. Explain (02)
(c) Define habit of a crystal with example. (02)

Q9. (a) What is hydrogen bonding. Explain role of hydrogen bonding in food and biological materials (04)
(b) Explain the structure of NaCl. Show that ratio of Na^+ and Cl^- ions in its unit cell is 1:1 (04)

Chapter 5

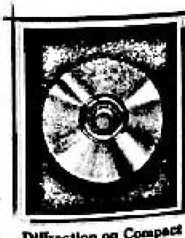
ATOMIC STRUCTURE



Albert Einstein

Neil Bohr

Continuous Spectrum



Diffraction on Compact Disc(CD) Surface

Line Emission Spectrum

Line Absorption Spectrum

CONTENTS

Chapter-5 **Atomic Structure**

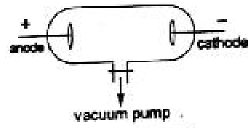
SUB-ATOMIC PARTICLES OF ATOM

- Matter is composed of very small particles called atom.
- According to Dalton's atomic theory, atom cannot be divided further.
- However, modern researches show that atom is divisible. Several sub-atomic particles like electron, proton and neutron have been discovered.

Discovery of Electron (Cathode Rays)

Gas Discharge Tube

- It is a glass tube having two metallic electrodes sealed into it.
- It may contain a gas, air or vapours of any substance at any pressure.
- It tube can be connected to a vacuum pump to maintain any low pressure.
- The electrodes are connected to a high voltage battery. The exact voltage required depends upon the length of the tube and the pressure inside it.
- A slit can be used in it to get a sharp beam of radiations.



Gas Discharge Tube

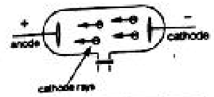
Example:

A 'neon sign' is also a discharge tube, which contain neon gas at a pressure of about 10 torr. Television and computer monitor screen are also gas discharge tubes called cathode ray tube (CRT)

Discovery of Electrons (or Cathode Rays)

William Crooks Experiment

In late 19th century, William Crooks studied the passage of electric current through gases. For this purpose, he used a gas discharge tube.



Production of cathode rays

Results of William Crooks Experiment

He obtained following results

- At normal pressure, gases do not conduct electricity even if the voltage is as high as 5000 volts.

- However, when the pressure inside the gas discharge tube is reduced and high voltage of 5000–10000 volts is applied, the gases begin to conduct electricity and a uniform glow appears inside the tube.
- When the pressure is further reduced to 0.01 torr, uniform glow disappears and fluorescence appears on the glass walls opposite to
- the cathode. This is actually due to the striking of some rays on the glass wall. These rays are called Cathode rays.
- The colour of the fluorescence depends upon the composition of glass.
- Different gases and vapours of different substances were used in the discharge tube. Also different metals were used as electrodes. But always same rays were produced.

Properties of Cathode Rays

1. Travel in a Straight Line

In 1869, Hittorf showed that Cathode rays travel in a straight line.

He found that cathode rays produce a sharp shadow of an opaque object placed in their path. It shows that these rays travel in a straight line, perpendicular to the surface of cathode.

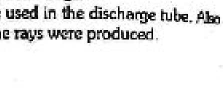


Figure: Cathode rays cast a shadow of an opaque object

2. Possess Momentum.

These rays can drive a small paddle wheel placed in their path. Cathode rays strike against the paddles of the paddle wheel and make it move.

This shows that cathode rays are actually beam of particles which have momentum (i.e. mass and velocity).

Figure: Cathode rays drive a small paddle wheel

Exercise Q4 (d):

The bending of the cathode rays in the electric and magnetic fields shows that they are negatively charged.

3. Negatively Charged

In 1895, J Perrin showed that cathode rays are negatively charged.

He found that when cathode rays are passed through a magnetic field, these are curved downward by the magnetic field.

Moreover, in 1897, J.J. Thomson showed that when cathode rays are passed through an electric field, these are deflected towards positively charged plate.

Figure: [illegible]

These experiments show that cathode rays are negatively charged.

4. Produce Fluorescence

They produce greenish fluorescence on striking the walls of the glass tube.

They also produce fluorescence in rare earths and minerals.

e.g. alumina glows red and tin stone glows yellow.

5. Produce X-rays

Cathode rays can produce X – rays, when strike an anode particularly with high atomic mass.

6. Possess Energy (Energetic Rays)

When cathode rays strike an object, it becomes heat up showing that cathode rays are energetic rays. When cathode rays from a concave cathode fall on a platinum foil, it begins to glow.

7. Ionize Gases

These can ionize gases by removing electron from them. Thus, positive ions are produced.

8. Cause Chemical Change

These are negatively charged. So, their addition cause reduction of a substance. Thus, these can cause a chemical change.

9. Pass through thin foil

These can pass through a thin metal foil like aluminium or gold foil.

10. Charge to mass (e/m) ratio

Their e/m ratio shows that they are simply electrons.

Conclusions

- J.J. Thomson proved that cathode rays are actually a stream of negatively charged particles. He calculated their e/m ratio. He found that the e/m ratio remains same for every gas used in the discharge tube. He concluded that these are fundamental particles of atom.
- Stoney called these rays as 'electrons'.

Discovery of Proton (Positive Rays)

In 1886, a German physicist, Eugein Goldstein discovered another type of rays called positive rays or canal rays, in the gas discharge tube.

Experiment

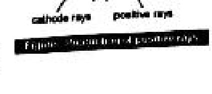


Figure: [illegible]

Eugein Goldstein used a perforate cathode in discharge tube. When a large voltage is applied, a glow appears on the glass wall opposite to anode. It is because some rays travel opposite to the cathode rays

and after passing through perforated cathode, they produce glow on the wall.

- Since these rays pass through the holes (canals) in the cathode, therefore, these are called canal rays.
- These rays are called positive rays since they carry positive charge.

How Canal Rays are Produced? (Origin of Positive Rays)

These rays are produced when high-speed cathode rays (electrons) strike the gas molecules present inside the gas discharge tube. Cathode rays remove electrons from the gas molecules and convert them into positive ions. These ions then move towards the cathode as positive ray.

$$M + e^- \longrightarrow \underset{\text{(Positive ray)}}{M^+} + 2e^-$$

Properties of Positive Rays

1. ***Travel in a straight line***

   These rays travel in a straight line in a direction opposite to the cathode rays.

2. ***Produce Flashes (Fluorescence)***

   They produce flashes on striking ZnS plate.

3. ***Positively Charged***

   These rays are deflected in an electric and magnetic field in a way that shows their positive charge.

4. ***Charge to mass (e/m) ratio***

   (i) The charge to mass ratio (e/m) for these rays is always smaller than for electrons.

   (ii) The e/m ratio depends upon the nature of the gas used in the gas discharge tube. Heavier the gas, smaller is the e/m value.

   (iii) The e/m ratio is highest when hydrogen is present. It is because, the positive particle obtained from hydrogen have least 'm' value. Hence its e/m ratio is highest.

Conclusions

- Hydrogen produces the lightest positive particle. Rutherford called this positive particle as proton. It is also considered as the fundamental particle of an atom.
- From e/m ratio of proton, the mass of proton was calculated to be 1.6726×10^{-27} kg or 1.0073 amu.
- The mass of proton is 1836 times greater than that of electron.

Protons and Electrons were discovered until 1886 and their properties were completely understood until 1895.

Exercise Q6. (a):

Discuss Chadwick's experiment for the discovery of neutrons.

Discovery of Neutron

Rutherford Prediction

In 1920, Rutherford predicted the presence of a neutral particle (neutron) in the nucleus of an atom. It is because the atomic masses of atoms could not be explained on the basis of protons and electrons only.

Chadwick's Experiment

- Chadwick discovered neutron in 1932. He was awarded Nobel Prize in Physics in 1935.
- Chadwick bombarded the nucleus of beryllium with α-particles (produced from polonium metal source) and found that it gave highly penetrating radiation. Charged detector showed these radiations as neutral. These radiations were called neutrons.

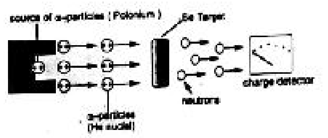


Figure: Bombardment of Be with α-particles and discovery of neutron

- Nuclear Reactions: This neutron was produced as

  Formation of α-Particle from Polonium

  $$^{216}_{84}Po \longrightarrow {}^{212}_{82}Pb + {}^{4}_{2}He \text{ (α-Particle)}$$

  Formation of Neutron

  $$^{4}_{2}He + {}^{9}_{4}Be \longrightarrow {}^{12}_{6}C + {}^{1}_{0}n \text{ (neutron)}$$

- Like electrons and protons, neutrons are also considered as a fundamental particle of atom.

Properties of Neutron

1. ***Cannot ionize gases***

   Neutron can not ionize gases because it is a neutral particle

2. ***Free Neutron Decays***

   Free neutron decays to give a proton with the emission of a neutrino and an electron.

$${}^{1}_{0}n \longrightarrow {}^{1}_{+1}P + {}^{0}_{-1}e + {}^{0}_{0}n$$

3. ***High Penetrating Power***

Neutrons have high penetrating power. They can knock out high-speed protons from paraffin, water, paper and cellulose.

4. ***Fast and Slow Neutrons***

- Neutrons travelling with 1.2 MeV energy are called fast neutrons
- Nutrons travelling with energy less than1 eV are called slow neutrons.
- Slow neutrons are more effective than fast ones for the nuclear fission process.

5. ***Carry out Nuclear reactions***

They can carry out nuclear reactions when used as projectiles.

Examples:

(i) a neutron can ejects an α-particle from the nucleus of nitrogen and boron is produced. ${}^{1}_{0}n + {}^{14}_{7}N \longrightarrow {}^{11}_{5}B + {}^{4}_{2}He$

(ii) Slow moving neutrons produce γ - radiations on striking Cu metal. In this process radioactive ${}^{66}_{29}Cu$ is converted into ${}^{66}_{30}Zn$. Neutron is captured by the nucleus of ${}^{65}_{29}Cu$ and ${}^{66}_{29}Cu$ is produced. This radioactive ${}^{66}_{29}Cu$ emits an electron (β– particle) and its atomic number is increased by one unit.

$${}^{1}_{0}n + {}^{65}_{29}Cu \longrightarrow {}^{66}_{29}Cu + h\nu_{(\gamma - radiations)}$$

$${}^{66}_{29}Cu \longrightarrow {}^{66}_{30}Zn + {}^{0}_{-1}e$$

6. Biological Activity:

These are used in the treatment of cancer due to their biological activity.

Particle	Charge (C)	Relative charge	Mass (kg)	Mass (amu)
Proton	$+1.6022 \times 10^{-19}$	+1	1.6726×10^{-27}	1.0073
Neutron	0	0	1.6750×10^{-27}	1.0087
Electron	-1.6022×10^{-19}	-1	9.1095×10^{-31}	5.4858×10^{-4}

Exercise Q5. (b):

What is J.J Thomson's experiment for determining e/m value of electron?

Measurement of Charge to Mass Ratio (e/m) of Electron

J.J Thomson determined the e/m ratio of cathode (electrons) rays in 1897. But he could not determine the charge or mass of the electrons separately.

- He subjected a beam of cathode rays to the simultaneous effects of electric and magnetic fields as shown in the figure.
  - ✓ In the absence of electric & magnetic field, the electrons strike at P_1.
  - ✓ When only magnetic field is applied, the electrons strike at P_2
  - ✓ When only electric field is applied, the electrons strike at P_3
- The strength of electric and magnetic field is so adjusted that the electrons strike at P_1
- Now from the comparison of the strengths of electric and magnetic fields e/m ratio is calculated.
- The calculated value of e/m is 1.7588×10^{11} Coulomb/kg.
- It means one kg of electron carries a charge of 1.7588×10^{11} Coulombs.

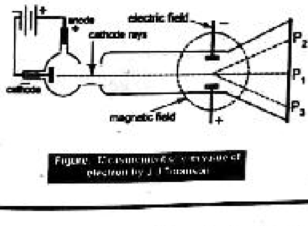


Figure: Measurement of e/m value of electron by J.J Thomson

Exercise Q5. (a):

Explain Millikan's oil drop experiment to determine the charge of an electron?

Measurement of Charge on Electron

(Millikan Oil Drop Experiment)

In 1909, R.A. Millikan determined the charge of an electron with the help of an apparatus as shown in the figure.

Figure: [illegible]

Construction

- It consists of a metallic chamber consisting of two parts.
- It also has two parallel electrodes in it.
- The upper electrode has a hole in it.
- The chamber is filled with air and its pressure can be

adjusted with a vacuum pump.

- The apparatus has an atomizer to introduce fine droplets into the chamber.
- It has a microscope and arc lamp to see the motion of droplets.
  The falling droplet is illuminated by the arc lamp perpendicular to the direction of view. Thus, it appears as bright speck (spot) against dark background.
- An X-ray generator is used to ionize the gas in the chamber.

Working

- Tiny droplets of oil are introduced into the chamber by an atomizer. Some droplets enter into the hole.
- Droplets fall under the action of gravity.
- Falling velocity of the droplets is directly proportional to its weight.

  i.e. $v_1 \propto mg$ ____ (1)

  where m = mass of droplet. g = acceleration due to gravity
- Now the air between the electrodes is ionised by X—rays. Oil droplets take electrons from the ionized air and become negatively charged.
- The electrodes are then connected to the an electric field of strength *E*. The oil droplets, being negatively charged, rises up towards the positively charged plates, against the force of gravity with velocity v_2.

  i.e. $v_2 \propto Ee - mg$ ______ (2)

  where e = charge on the droplet.
- Divide eq (1) by (2)

  $$\frac{v_1}{v_2} = \frac{mg}{Ee - mg} \quad \text{\_\_\_\_ (3)}$$
- The strength of the electric field is so adjusted that the droplet becomes stand still. Under this condition, mass of the droplet (*m*) can be determined.
- Thus if v_1, v_2, *E*, *g* and *m* are known, charge on the droplet can be determined using equation (3)

Conclusions

- Millikan determined charge on many oil droplets and found that it was always 1.59×10^{-19} C or some multiple of it.
- The least charge 1.59×10^{-19} C on oil droplet is because when it picks up one electron from the air in the chamber. This value is very close to the modern value of charge which is 1.6022×10^{-19} C. <u>Thus charge on one electron = 1.6022×10^{-19} C</u>
- This charge present on an electron is the smallest charge of electricity that has been determined so far.

Exercise Q5. (c):

Evaluate mass of electron from the above two experiments.

Determination of Mass of Electron

From e/m ratio of electrons, mass of electron can be calculated as

Since

$$\frac{e}{m} = 1.7588 \times 10^{11}\,C/Kg$$

$$m = \frac{e}{1.7588 \times 10^{11}}$$

$$m = \frac{1.6022 \times 10^{-19}\,C}{1.7588 \times 10^{11}\,C\,kg^{-1}}$$

$$m = 9.1096 \times 10^{-31}\,kg$$

Exercise Q6. (b):

Rutherford's atomic model is based on the scattering of α-particles from a thin gold foil. Discuss it and explain the conclusions.

RUTHERFORD'S MODEL OF ATOM (DISCOVERY OF NUCLEUS)

α-scattering experiment

- In 1911, Lord Rutherford bombarded a thin gold foil 0.00004 cm thickness with high-speed α - particles, coming from a radioactive material (radium or polonium).
- A beam of α-particles was obtained by using a pinhole in lead sheet. A photographic plate or a screen coated with ZnS was used as a detector. When α -particles struck the screen, flashes of light were produced.
- Rutherford observed that most of the particles went straight through the foil.
- A few were deflected at various angles and some were deflected backward.

Conclusions

1. Since most of the α-particles went straight, therefore, most of the space in an atom is empty.
2. The central heavy region, which deflects the α-particles, must have heavy positive charge. This part of the atom is called Nucleus.
3. Nucleus occupies very small volume of the atom. Remaining volume of the atom is occupied by extra nuclear moving electrons.

Rutherford's Atomic Model

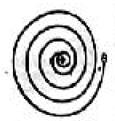
Based on α – scattering experiment, Rutherford proposed a planetary model of atom in 1911. This model was similar to solar system.

Postulates

1. An atom consists of a nucleus containing positive charge and practically the whole of its mass.
2. The nucleus is surrounded by a number of electrons equal to the number of protons in the nucleus.
3. The electrons are in constant motion around the nucleus in closed orbit like that of planets around the sun. The centrifugal force is balanced by the electrostatic force of attraction between the electrons and nucleus. Thus, electrons revolve around the nucleus.

Defects

1. Rutherford's model is based upon laws of motion and gravitation. These laws can be easily applied to neutral bodies but not to the charged bodies such as electrons and protons.
2. A revolving electron must emit energy continuously. As a result, electron will move in a spiral path and will fall into the nucleus. Thus, whole atom would collapse. However, it never happens.
3. If electron emits energy continuously, then a continuous spectrum should be formed. Actually, atoms form line spectrum.



PLANCK'S QUANTUM THEORY

In 1900, Max Planck proposed quantum theory of light to explain emission and absorption of radiations. According to his theory, energy travels in a discontinuous manner. It is composed of large number of tiny discrete (separate) units called quanta.

Postulates of Planck's Quantum theory

1. Energy is not emitted or absorbed continuously. It is emitted or absorbed in a discontinuous manner in the form of wave packets called quanta. In case of light the quantum of energy is often called photon.
2. Each wave packet or quantum has a definite amount of energy.
3. A body can emit or absorb energy only in terms of quanta.
4. The energy of the quantum is directly related to the frequency of radiation by the equation

$E \propto \nu$

or $E = h\nu$ ________ (1)

where E = Energy of the quantum ν = Frequency of radiation

h = Planck's constant $= 6.625 \times 10^{-34}$ Js

Properties of Waves

Frequency

It is the number of waves, which passes through a given point in one second.

It is denoted by ν. Its units are cycles s^{-1} or s^{-1} or Hertz (Hz).

1 Hz = 1 cycles s^{-1}

It is related to wavelength as

$c = \nu\lambda$ or $\nu = c/\lambda$ ________ (2)

Where c = velocity of light $= 3 \times 10^{8}\ ms^{-1}$

λ = wavelength of any light radiation

Wave Length

It is the distance between two adjacent crests or troughs in a beam of radiation.

It is denote by λ.

Its units are meter, nanometre or angstrom etc.

$1\ A^{\circ} = 10^{-10}$ m, 1 nm $= 10^{-9}$ m, 1 pm $= 10^{-12}$ m

Put eq. 2 in eq. 1

$E = hc/\lambda$ ________ (3)

λ is related to the wave number i.e.; $\bar{\nu}$ as

$\lambda = 1/\bar{\nu}$ ________ (4)

Wave Number

It is the number of waves per unit distance.

It is denoted by $\bar{\nu}$. Its units are m^{-1} or cm^{-1} etc.

Put eq. 4 in eq. 3

$E = hc\bar{\nu}$ ______ (5)

- Equations 1, 3 and 5 shows that energy of light is directly proportional to its frequency and wave number but inversely proportional to its wavelength.
- Greater the wave number of photons, greater is the energy associated with them
- The relationships of energy, frequency, wavelength, wave number about the photon of light are accepted by scientists and used by Bohr in his atomic model.

Exercise Q7. (a):

Give the postulates of Bohr's atomic model. Which postulate tells us that orbits are stationary and energy is quantized?

THE BOHR ATOMIC MODEL

In 1913, Bohr proposed a model of atom which removed the defects of Rutherford's atomic model and explained the spectrum of hydrogen atom. Bohr used Planck's quantum theory and proposed that electrons are present in hydrogen atom in certain quantized energy levels.

Postulates of Bohr's Atomic Model

1. Electron revolves outside the nucleus in circular orbits. Each orbit has fixed energy and a quantum number.
2. Electron does not radiate energy as long as it remains in a fixed orbit. Energy is emitted or absorbed only when an electron jumps from one orbit to another orbit.
3. The electron emits energy when it jumps from an outer to an inner orbit and absorbs energy when it jumps from an inner to an outer orbit.

   When an electron jumps, the energy change ΔE is given by

   $$\Delta E = h\nu = E_2 - E_1$$
4. Electron can revolve only in those orbits, which have fixed value of angular momentum (mvr). The angular momentum of an electron in any orbit is an integral multiple of $h/2\pi$.

   $$\text{Angular momentum} = mvr = \frac{nh}{2\pi}$$

   where n = principal quantum number and its value is 1, 2, 3...
   v = velocity of electron r = radius of the electronic orbit
   m = mass of electron h = Planck's constant = 6.625×10^{-34} Js.

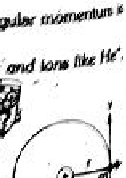
   Thus, the permitted values of angular momenta are $\frac{h}{2\pi}, \frac{2h}{2\pi}, \frac{3h}{2\pi}$ etc. Hence, electron is present only in any one of these orbits and not in between them, i.e., angular momentum is quantized.

Based on these assumptions, Bohr presented a model of hydrogen atom and ions like He^+, Li^{2+} etc.

Exercise Q7. (b):

Derive the equation for the radius of nth orbit of hydrogen atom using Bohr's model.

Radius of Orbits



Consider an electron of mass 'm', and charge 'e^-', moving in a circular orbit of radius 'r', with velocity 'v' around the nucleus of charge 'Ze^+'. The 'Z' is the proton number (atomic number) and

'e^+' is the charge on proton.

According to Coulomb's law

The force of attraction between two charged bodies is directly proportional to the product of the magnitude of their charges, and inversely proportional to the square of distance between them.

Thus for two charges Q_1, Q_2 separated by distance r

$$F = \frac{Q_1Q_2}{4\pi\varepsilon_0 r^2}$$

→ The columbic force of attraction between the nucleus and the electron provides the centripetal force for the motion of electron. It is given by

$$F = \frac{Ze.e}{4\pi\varepsilon_0 r^2} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \quad \text{------} \quad (1)$$

where $1/4\pi\varepsilon_0$ = Coulomb's law constant.

ε_0 is the vacuum permittivity. Its value is $8.84 \times 10^{-12}\ C^2J^{-1}m^{-1}$

→ The centrifugal force acting on the electron is given by

$$F = \frac{mv^2}{r} \quad \text{------} \quad (2)$$

→ For uniform circular motion, the centripetal and the centrifugal forces balance each other. Thus

$$\frac{mv^2}{r} = \frac{Ze^2}{4\pi\varepsilon_0 r^2}$$

So, the equation for velocity of an electron in any orbit is

$$v^2 = \frac{Ze^2}{4\pi\varepsilon_0 r\, m} \quad \text{------} \quad (3)$$

This eq shows that square of velocity of electron is inversely proportional to the radius of orbit. It means electrons revolve faster in an orbit of smaller radius nearer to the nucleus. As the electron moves to higher orbits of larger radius, its velocity decreases.

→ According to Bohr's postulate

$$mvr = n\frac{h}{2\pi}$$

$$v = \frac{nh}{2\pi mr}$$

Squaring on both sides

$$v^2 = \frac{n^2h^2}{4\pi^2m^2r^2} \quad \text{------- (4)}$$

Comparing eq. 3 and eq. 4 , we get

$$\frac{Ze^2}{4\pi\varepsilon_0 rm} = \frac{n^2h^2}{4\pi^2m^2r^2}$$

or

$$r = \frac{\varepsilon_0 n^2h^2}{\pi m Ze^2}$$

$$r = \frac{\varepsilon_0 h^2}{\pi m e^2} \times \frac{n^2}{Z}$$

$$r = (a_0) \times \frac{n^2}{Z}$$

$\boxed{1\,\text{Å} = 10^{-10}\,\text{m}}$

where

$$a_0 = \frac{\varepsilon_0 h^2}{\pi m e^2} = \text{constant}$$. Its value is 5.29×10^{-11} m or 0.529 Å

→ For hydrogen, Z= 1, therefore

$$r = a_0 \times n^2$$

So, the equation for radius of orbits 'n' in an hydrogen atom is

$$r = 0.529 \times n^2$$

This eq. shows that radius of the orbit is directly proportional to the square of orbit number. Hence higher orbits have more radii and vice versa. It means that radius of orbits goes on increasing with increasing orbit numbers.

→ *Examples:*

For n = 1 $\quad r = 0.529 \times 1^2 = 0.529$ Å

For n = 2 $\quad r = 0.529 \times 2^2 = 2.11$ Å

For n = 3 $\quad r = 0.529 \times 3^2 = 4.75$ Å

For n = 4 $\quad r = 0.529 \times 4^2 = 8.4$ Å

For n = 5 $\quad r = 0.529 \times 5^2 = 13.22$ Å

Thus radius of orbits goes on increasing with increasing orbit numbers. The orbits are not equally spaced.

Hence, we have $r_2 - r_1 < r_3 - r_2 < r_4 - r_3 < \ldots$

The second orbit is four times away from the nucleus than first orbit, third orbit is nine times away and fourth orbit is sixteen times away.

Exercise Q8:

Drive the formula for calculating the energy of an electron in nth orbit using Bohr's model. Keeping in view this formula explain the followings:

Energy of the Revolving Electron

The total energy of an electron in an orbit is equal to the sum of its K.E. due to its motion and P.E. due to electrostatic interaction with the nucleus.

i.e. $\quad$ E=K.E. + P.E.

→ ***Kinetic Energy***

K.E. is given by

$$K.E = \frac{1}{2}mv^2$$

$$K.E. = \frac{1}{2}m\frac{Ze^2}{4\pi\varepsilon_0 r\, m} \qquad \text{since } v^2 = \frac{Ze^2}{4\pi\varepsilon_0 rm} \text{ from eq.(3)}$$

or $$K.E. = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

→ ***Potential Energy***

Work done is given by

Work = Force × distance

The electrostatic force of attraction between the nucleus and the electrons is the coloumbic force $= \frac{Ze^2}{4\pi\varepsilon_0 r^2}$. If the electron moves through a small distance dr, the the work done for moving electron is given by

$$\text{work} = \frac{Ze^2}{4\pi\varepsilon_0 r^2} \times dr \qquad (\text{work} = \text{force} \times \text{distance})$$

In order to calculate the total P.E. of electron at a distance 'r' from the nucleus, total work done is calculated in bringing electron from infinity to distance 'r'. Thus above eq. is integrated between the limits infinity and r

Thus $$P.E. = \int_{\infty}^{r} \frac{Ze^2}{4\pi\varepsilon_0 r^2}\, dr$$

$$P.E. = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

The minus sign indicates that the P.E. decreases when the electron is brought from infinity to distance 'r'. At infinity, the electron is not attracted by any thing, thus P.E. is zero. At a point nearer to the nucleus, electron is attracted by nucleus, thus P.E. is less than zero.

→ Thus

Total energy = E = K.E. + P.E.

$$E = \frac{Ze^2}{8\pi\varepsilon_0 r} - \frac{Ze^2}{4\pi\varepsilon_0 r}$$

$$E = \frac{Ze^2}{\pi\varepsilon_0 r}\left(\frac{1}{8} - \frac{1}{4}\right)$$

$$E = -\frac{Ze^2}{8\pi\varepsilon_0 r} \quad \text{———— (6)}$$

→ On substituting the value of '*r*' from equation (5) in eq. (7) we get

$$E = -\frac{Ze^2}{8\pi\varepsilon_0 \dfrac{\varepsilon_0 n^2h^2}{\pi m Z e^2}}$$

$$\boxed{\textbf{Since} \quad r = \frac{\varepsilon_0 n^2 h^2}{\pi m Z e^2} \quad \textbf{from eq. (5)}}$$

Or
$$E_n = -\frac{mZ^2e^4}{8\varepsilon_0^2 n^2 h^2} \quad \text{—— (7)}$$

Where E_n is the energy of the electron in nth orbit.

→ Putting the values of **m, e, ε_0 h**

$$E = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2} \; J$$

For hydrogen atom Z=1. Thus

$$E = -2.18 \times 10^{-18} \times \frac{1}{n^2} \; J$$

→ The value of energy associated with 1 mole of H (i.e. 1.008 g) will be

$$E_n = -2.18 \times 10^{-18} \times \frac{1}{n^2} \times \frac{6.02 \times 10^{23}}{1000}$$

or
$$E_n = -\frac{1313.31}{n^2} \; kJ/mol$$

Hence

For n=1 $\quad E_1 = -\frac{1313.31}{1^2} = -1313.31 \; kJ/mol$

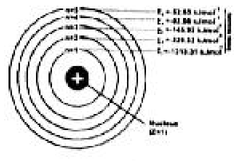
For n=2 $\quad E_2 = -\frac{1313.31}{2^2} = -328.32 \; kJ/mol$

For n=3 $\quad E_3 = -\frac{1313.31}{3^2} = -145.92 \; kJ/mol$

For n=4 $\quad E_4 = -\frac{1313.31}{4^2} = -82.08 \; kJ/mol$

For n= 5 $\quad E_5 = -\frac{1313.31}{5^2} = -52.53 \; kJ/mol$

For n= ∞ $\quad E_\infty = -\frac{1313.31}{\infty^2} = 0 \; kJ/mol$ (i.e. electron is free from the nucleus)



Thus, value of energy goes on increasing towards higher orbits.

→ The energy differences between adjacent orbits are

$E_2 - E_1 = (-328.32) - (-1313.31) = 984.99$ kJ/mol

$E_3 - E_2 = (-145.92) - (-328.32) = 182.40$ kJ/mol

$E_4 - E_3 = (-82.08) - (-145.92) = 63.84$ kJ/mol

Thus, difference of energy between adjacent energy levels goes on decreasing.

i.e. $E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > \ldots$

→ The energy difference between first and infinite energy level is given as

$E_\infty - E_1 = (0) - (-1313.31) = 1313.31$ kJ/mol

It is the ionization energy of the hydrogen. This value agrees well with the experimental value.

SPECTRUM

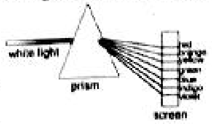
A visual display or dispersion of the components of white light, when it is passed through a prism is called a spectrum.

Examples:

Spectrum of White Light:

Light from sun and electric bulb consists of radiations of different wavelengths.

When this light is passed through a prism, it is separated into a band of different colours. It is because, the light of longer wavelengths bend to a smaller degree while



the light of shorter wavelengths bend to a greater degree and thus different colours are obtained as shown in the figure.

Electromagnetic Spectrum:

(Visible and Invisible Spectrum)

There are seven regions in electromagnetic spectrum. One is the visible region. The spectrum of white light is visible to the naked eye & is known as visible spectrum. Its range is from 400 nm to 800 nm.

Others are:

- The rays having wavelengths below violet are Ultraviolet, X-rays and γ-rays. These have photons with greater energy.
- Above red are infrared, microwaves and radio waves. All these are not visible to the naked eye.
- These rays form the invisible spectrum.

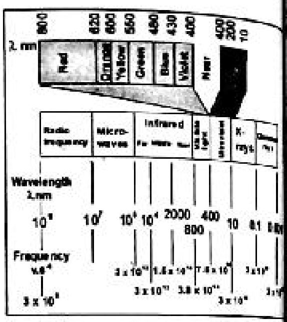


Figure: The visible and other regions of spectrum

Types of Spectrum

There are two types of spectrum

(i) Continuous Spectrum e.g. Rainbow

(ii) Line Spectrum e.g. Atomic Spectrum

(i) Continuous Spectrum

The spectrum in which rays of different wavelengths diffuse into one another and no definite boundary can be drawn between them is called continuous spectrum.

Example: Rainbow

It is obtained from the light emitted by the sun or incandescent (electric light) solids. It is the property of matter in bulk.

Exercise Q10. (c):

What is the origin of line spectrum?

(ii) Line Spectrum (Or Atomic Spectrum)

The spectrum in which dark or bright lines are separated by bright or dark spaces is called line spectrum.

Origin of Line Spectrum

Line spectrum is characteristic of an atom. When an element or its compound is volatilized on a flame, it emits light. When this light is seen through a spectrometer, distinct lines are seen separated by dark spaces. The number of lines and distance between them depends upon the nature of element.

Examples:

(i) Line spectrum of Na consists of two yellow lines separated by a definite distance.

(ii) Similarly, the spectrum of hydrogen consists of a number of lines of different colours separated by definite distances. In hydrogen atom spectrum, distance between lines decreases with decrease in wavelength and after certain wavelength, the spectrum becomes continuous.

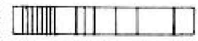


Figure: Atomic spectrum of hydrogen

Types of Atomic or Line Spectrum

Atomic Spectrum can be of two types.

(i) *Atomic absorption spectrum*

(ii) *Atomic emission spectrum*

Line Absorption Spectrum or Atomic Absorption Spectrum.

In this, dark lines are separated by bright bands.

Example: (Origin of Line [Atomic] Absorption Spectrum)

When white light is passed through a sample of a substance, it may absorb particular radiations. This light on passing through prism will form a spectrum in which dark lines will be present in place of absorbed radiations.

It has been shown in the fig.

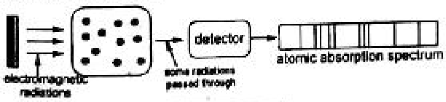


Figure: Atomic absorption spectrum

Line Emission Spectrum or Atomic Emission Spectrum.

In this, bright lines are separated by dark bands.

Example (Origin Of Atomic Emission Spectrum)

When a substance is heated or subjected to electric discharge, it emits radiations of definite wavelengths. These radiations will produce bright lines on a dark screen as shown in the figure.

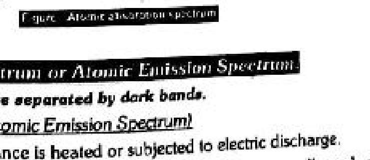


Figure: Atomic emission spectrum

NOTE

- The position or wavelength of lines in both emission and absorption spectrum of an element is same.
- In emission spectrum, the lines appear bright while in absorption spectrum these lines appear black.

Exercise Q10. (a):

What is spectrum. Differentiate between continuous spectrum and line spectrum.

	Continuous Spectrum		Line Spectrum
1	In this, coloured are diffused into each other and they are not separated.	1	It consists of dark or bright lines separated by bright or dark bands.
2	Each colour in the band has a range of frequencies.	2	Each line in the spectrum has its own characteristic colour and frequency.
3	There is not sharp boundary between the colours.	3	There is distance between the lines.
4	It is characteristic of the molecules.	4	It is characteristic of atoms.
5	It is obtained by passing polychromatic light through a triangular prism.	5	It is obtained by heating a substance or by passing polychromatic light through a substance and then passing emitted radiations through a prism.
6	It has only one type	6	It is of two types (i) line emission spectrum (ii) line absorption spectrum
7	Example Rainbow	7	Example Blamer series of hydrogen spectrum.

Exercise Q10. (b):

Compare line emission and line absorption spectra.

	Line Emission Spectrum Or (Atomic Emission Spectrum)		Line Absorption Spectrum Or (Atomic Absorption Spectrum)
1	In this bight lines are separated by dark bands.	1	In this dark lines are separated by bright bands.
2	It is formed when the substance is in excited state.	2	It is formed when the substance is in unexcited state.
3	It is formed when the substance is excited to vapour state	3	It is formed by transparent gases, transparent liquids and solids.
4	For its formation electron jumps from higher energy level to lower energy level and emit energy as light. The emitted radiations are indicated by coloured lines.	4	For its formation electron jumps from lower energy level to higher energy level by absorbing energy. The absorbed radiations are indicated by dark lines.
5	Emission spectrum of sodium has two yellow lines separated by dark bands.	5	Absorption spectrum of sodium has two dark lines separated by bright bands.

Emission Spectrum of Hydrogen

When hydrogen is filled in a discharge tube at a very low pressure, it emits bluish light. This light when seen with spectrometer shows many lines called spectral lines. These lines can be classified into five groups called spectral series.

i) **Lyman series** (U.V. region)

ii) **Balmer series**(Visible region)

iii) **Paschen series**(I.R. region)

iv) **Brackett series**(I.R. region)

v) **Pfund series**(I.R. region)

First four series were discovered before Bohr's atomic model. The wave number of spectral lines decreases from Lyman to Pfund series. The lines of Balmer series have been given specific names as H_α , H_β ... etc.

Table: Wave numbers of various series of hydrogen spectrum				
Lyman series (U.V. region)	Balmer series (Visible region)	Paschen series (I.R. region)	Bracket series (I.R. region)	Pfund series (I.R. region)
82.20×10^5	15.21×10^5 (H_α line)	5.30×10^5	2.46×10^5	1.34×10^5
97.60×10^5	20.60×10^5 (H_β line)	7.80×10^5	3.80×10^5	2.14×10^5
102.70×10^5	23.50×10^5 (H_γ line)	9.12×10^5	4.61×10^5	
105.20×10^5	24.35×10^5 (H_δ line)	9.95×10^5		
106.20×10^5	25.18×10^5			
107.10×10^5				

Origin Of Hydrogen Spectrum On The Basis Of Bohr's Model

According to Bohr's theory, when hydrogen atom is heated or subjected to electric discharge, its electron moves from lower orbit 'n_1' to higher orbit 'n_2'. When this electron comes back, it emits same energy in the form of photon of light.

Five series of spectral lines are present in hydrogen atom spectrum.

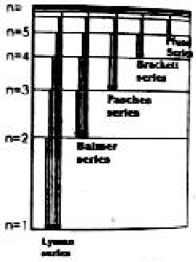


Figure: Series of spectral lines in H-atom spectrum

Series Name	n_1	n_2	Region of Spectrum
Lyman series	1	2, 3, 4...	ultraviolet
Balmer series	2	3, 4, 5...	visible
Paschen series	3	4, 5, 6...	infrared
Brackett series	4	5, 6, 7...	infrared
Pfund series	5	6, 7, 8...	infrared

Exercise Q9. (a): *Derive the following equations for hydrogen atom which are related to:*

(i) Energy difference between two levels, n_1 and n_2.

(ii) Frequency of photon emitted which an electron jumps from n_2 to n_1.

(iii) Wave number of the photon when the electron jumps from n_2 to n_1.

Calculation of Wave Numbers of Photons of Various Spectral Series by Bohr's Theory

Energy of Photon

→ According to Bohr's postulate, an electron emits energy in the form of photon when it jumps from higher energy orbit to lower energy orbit such that

$$\Delta E = h\nu = E_2 - E_1$$

→ Let energy of electron in higher energy orbit n_2 is

$$E_2 = -\frac{mZ^2e^4}{8\varepsilon_0^2 n_2^2 h^2}$$

and, energy of electron in lower energy orbit n_1 is

$$E_1 = -\frac{mZ^2e^4}{8\varepsilon_0^2 n_1^2 h^2}$$

So,

$$\Delta E = E_2 - E_1 = -\frac{mZ^2e^4}{8\varepsilon_0^2 n_2^2 h^2} - \left(-\frac{mZ^2e^4}{8\varepsilon_0^2 n_1^2 h^2}\right) J$$

So

$$\Delta E = -\frac{mZ^2e^4}{8\varepsilon_0^2 n_2^2 h^2} + \frac{mZ^2e^4}{8\varepsilon_0^2 n_1^2 h^2}$$

$$\Delta E = \frac{mZ^2e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

→ Since for hydrogen atom Z=1, therefore

$$\Delta E = 2.18 \times 10^{-18} J\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) J$$

Frequency of Photon

→ Since $\Delta E = h\nu$

Therefore

$$h\nu = \frac{mZ^2e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\nu = \frac{mZ^2e^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) Hz$$

This eq shows that the frequency of photon emitted goes on decreasing between adjacent levels as we move towards higher orbits.

Wave Number of Photon

→ Since $c = \nu\lambda$ or $\nu = \frac{c}{\lambda}$ and $\lambda = \frac{1}{\bar{\nu}}$, therefore $\nu = c\bar{\nu}$, *Hence*

$$c\bar{\nu} = \frac{mZ^2e^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

→ For hydrogen atom Z=1

$$\bar{v}=\frac{me^4}{8\varepsilon_0^2ch^3}\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)m^{-1}$$

where $R=\frac{me^4}{8\varepsilon_0^2ch^3}=1.09678\times10^7\,m^{-1}$ = Rydberg constant

Exercise Q9 (b):

Justify that Bohr's equation for the wave number can explain the spectral lines of Lyman, Balmer and Paschen series.

Calculations of Wave numbers Of Various Lines Present In H-Atom Spectrum

Bohr's theory can be used to calculate the wavenumbers of spectral series of emission spectrum of hydrogen atom.

Lyman Series

First line $n_1=1$ (lower orbit) & $n_2=2$ (higher orbit)

$$\bar{v}=1.09678\times10^7\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=1.09678\times10^7\left(\frac{1}{1^2}-\frac{1}{2^2}\right)=82.26\times10^5\,m^{-1}$$

Second line $n_1=1$ & $n_2=3$

$$\bar{v}=1.09678\times10^7\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=1.09678\times10^7\left(\frac{1}{1^2}-\frac{1}{3^2}\right)=97.49\times10^5\,m^{-1}$$

Limiting line $n_1=1$ & $n_2=\infty$

$$\bar{v}=1.09678\times10^7\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=1.09678\times10^7\left(\frac{1}{1^2}-\frac{1}{\infty^2}\right)=109.678\times10^5\,m^{-1}$$

The limiting line of Lyman series lies in UV region.

Balmer Series

First line $n_1=2$ & $n_2=3$

$$\bar{v}=1.09678\times10^7\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=1.09678\times10^7\left(\frac{1}{2^2}-\frac{1}{3^2}\right)=15.234\times10^6\,m^{-1}$$

Second line $n_1=2$ & $n_2=4$

$$\bar{v}=1.09678\times10^7\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=1.09678\times10^7\left(\frac{1}{2^2}-\frac{1}{4^2}\right)=20.566\times10^5\,m^{-1}$$

Third line $n_1=2$ & $n_2=5$

$$\bar{v}=1.09678\times10^7\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=1.09678\times10^7\left(\frac{1}{2^2}-\frac{1}{5^2}\right)=23.00\times10^5\,m^{-1}$$

Limiting line $n_1=2$ & $n_2=\infty$

$$\bar{v}=1.09678\times10^7\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right)=1.09678\times10^7\left(\frac{1}{2^2}-\frac{1}{\infty^2}\right)=27.421\times10^5\,m^{-1}$$ The

Limiting line of Balmer series lies in U.V. region, while other lines fall in visible region.

- Similarly wave numbers of other series of lines i.e. Paschen, Brackett and Pfund series can also be calculated.
- Thus, Bohr's theory explained the spectrum of hydrogen atom.

Exercise Q13:

Point out the defects of Bohr's model. How these defects are partially covered by dual nature of electron and Heisenberg's uncertainty principle?

Defects of Bohr's Atomic Model

Bohr's theory explains the stability of atom, ionization energy and the spectra of hydrogen and hydrogen like atoms containing one electron e.g. He^+, Li^{2+}, Be^{3+} etc.

It has following defects

(i) It can not explain the spectrum of multi-electron systems like He, Li, Be etc

(ii) High resolving spectrometer shows that individual lines in line spectrum of an atom actually consist of several lines. e.g. H_α-line in Balmer series consists of five component lines. This is called fine structure or multiple lines. Bohr's theory cannot explain this fine structure. Splitting of lines shows that only principle quantum number is not sufficient. Azimuthal quantum explains the splitting of of spectral lines.

(iii) Bohr suggested circular orbits for electrons. However, researches have shown that the motion of electron around the nucleus takes place in three dimensional space. Thus atomic model is not flat

(iv) When the spectrum of atom is taken in the magnetic field, some new lines are created. This is called Zeeman effect. e.g. when Na spectrum is taken in a weak magnetic field, its single line is split up into two component lines.

Similarly, when emission spectrum of excited H-atom is taken in an electrical field, lines are split up into component lines. This is called stark effect.

Bohr's theory cannot explain Zeeman effect and Starks effect.

Sommerfeld modification of Bohr Atomic model

To explain Zeeman and Stark effect, Sommerfeld suggested in 1915 that electrons revolve in elliptical orbits rather than in circular orbit.

In this model, nucleus is present at one of the foci of the ellipse. The elliptical path of electron goes on changing in space and thus nucleus is covered by the electron cloud from all sides.

Exercise Q12. (a):

What are X-rays? What is their origin? How was the idea of atomic number derived, from the discovery of X-rays?

X-RAYS AND ATOMIC NUMBER

When fast moving electrons strike a heavy metal anode surface in a discharge tube, some highly energetic rays are produced. These rays are called X-rays.

Origin of X-rays

In a gas discharge tube, electrons produced by heated tungsten filament are accelerated by high voltage. This gives them sufficient energy. Thus, when an electron suddenly stops on collision, energy is released in the form of electromagnetic waves called X-rays.

The wavelength of X-rays depends upon the nature of the target material. Every metal has its own characteristic X-rays.

Analysis of X-rays

When X-rays are generated, they emit in all directions. These are passed through a slit and then through aluminium window. These are then thrown on a crystal of $K_4[Fe(CN)_6]$, which analyze the X-rays. The rays are diffracted from the crystal and a line spectrum of X-rays is obtained. This is taken on a photographic plate. This X – ray spectrum is characteristic of the target material. This spectrum has discrete spectral lines. These lines are grouped into K–series, L–series and M–series. Each series has various lines as K_α, K_β, L_α, L_β, M_α, M_β etc.

Moseley's Law: Relationship of Atomic Number with X-rays

It states,

The frequency of a spectral line in X-ray spectrum varies as the square of atomic number of the element emitting it.

$$\sqrt{v} = a(Z - b)$$

This linear equation is the Moseley's Law.

where v = frequency of emitted X-rays, Z = atomic number of element

a = proportionality constant, b = screening constant of the metals

If $\sqrt{v}$ for K - series is plotted against Z, a straight line is obtained.

This law shows that physical and chemical properties of an element depend upon atomic number and not on atomic mass. Hence, Modern periodic table is based upon atomic number.

Moseley's Experiment

In 1913 – 1914, an English Scientist, *Moseley* studied the X-rays emitted by various metals. He used 38 different elements from Aluminium to Gold as target and covered a wavelength range of 0.04 – 8 A°. He obtained many useful results.

Results of Moseley's Research

1. The emitted rays are classified into two groups
   (a) One with shorter wavelengths are called K – series, and
   (b) One with longer wavelengths are called L – series.
2. Wavelength of emitted X-rays decreases with increase in atomic number of target material.
3. The relationship between frequency (v) of a particular line in X-rays and atomic number of the element is given by

Importance of Moseley's Law

(i) Moseley arranged K and Ar, Ni and Co in a proper way in Mendeleev periodic table.
(ii) This law has led to the discovery of many elements e.g. Tc (43), Pm(61), Rh(45)
(iii) The atomic number of rare earths have been determined by this law

WAVE-PARTICLE NATURE OF MATTER (DUAL NATURE OF MATTER)

de Broglie Hypothesis

Einstein and Plank showed that light has both wave-like and particle-like properties.

In 1924, a French scientist, Louis de Broglie, said that all matter particles in motion also have wave-like properties. Thus, electron, proton, neutron, atoms and molecules all have both particle and wave like properties. This is called wave-particle duality.

He obtained a relationship between the wavelength and the momentum of the particle, by using Einstein & Planck equations.

Einstein eq.is

$$E = mc^2 \quad \text{———} \quad (1)$$

Plank's eq.is

$$E = hv \quad \text{———} \quad (2)$$

Comparing eq. (1) and (2)

$$mc^2 = h\nu$$

$$mc^2 = \frac{hc}{\lambda} \quad , \quad \text{Since } \nu = c/\lambda$$

$$mc = \frac{h}{\lambda}$$

$$\lambda = \frac{h}{mc}$$

For a particle of mass (m) & velocity (v) the de Broglie equation will be

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

where p = mv = momentum of particle, h = Plank's constant = 6.625×10^{-34} J s

This equation shows that

- Particle has both wavelength (λ) and momentum. i.e., it has both wave and particle properties. Thus, it has dual nature.
- The wavelength of particle is inversely proportional to its momentum.

Examples

- Consider an electron moving with velocity 2.188×10^6 m s^{-1}. Its wavelength can be calculated as

Mass of electron $= m = 9.108 \times 10^{-31}$ kg

Planck's constant $= h = 6.625 \times 10^{-34}$ J s

Velocity of electron $= v = 2.188 \times 10^6$ m s^{-1}

Wavelength $= \lambda = ?$

Hence

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{9.108 \times 10^{-31} \times 2.188 \times 10^6}$$

$$\lambda = 0.33 \times 10^{-9} \text{ m}$$

Or $\lambda = 0.33$ nm , Since 1 nm $= 10^{-9}$ m

- This wavelength of moving electron of first orbit of H-atom is similar to that of X-rays and can be measured.
- For a proton moving with the same velocity, wavelength would be 1836 times smaller than that of electron.

- Similarly, an α – particle moving with same velocity would have wavelength, 7344 times smaller than that of electron.
- Now consider a mass of 0.001 kg (1 g) moving with a velocity of 10 m/s, its wavelength will be

$$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34}}{0.001 \times 10}$$

$$\lambda = 6.625 \times 10^{-32} \text{ m}$$

This wavelength is much shorter. It cannot be measured by any method.

Thus, heavier bodies also have wavelength but their wavelength can not be measured. Thus, it is said that heavier bodies do not have waves.

Experimental Verification of Dual Nature of Matter

Davisson and Germer Experiment

In 1927, two American scientists, Davisson and Germer gave experimental verification of the wave nature of electron.

They bombarded a thin Ni foil with fast moving electrons. Electrons are obtained from heated tungsten filament and accelerated by the potential difference through the charged plates. They observed that electron's diffraction was similar to the X – rays diffraction.

Moreover, they experimentally calculated the wavelength of electron, which was similar to that calculated theoretically using de-broglie eq.

Thus, Davisson and Germer verified de-broglie's eq. and dual nature of electron.

- Davisson and Germer got Nobel Prize for inventing apparatus to prove the matter waves.
- De-Broglie also got separate Noble prize for giving the equation of matter waves.

HEISENBERG'S UNCERTAINTY PRINCIPLE

It was given by Werner Heisenberg in 1927. It states

It is impossible to determine simultaneously and precisely, both position and momentum of a small fast moving particle e.g. electron.

Explanation

It means the more we certain about the position of a particle, the less will be the certainty about its momentum and vice versa.

Let uncertainty in position is Δx and uncertainty in momentum is Δp, then according to Heisenberg

$$\Delta x.\Delta p \geq \frac{h}{4\pi}$$

To satisfy this eq., it is clear that if uncertainty in position i.e., Δx is small, uncertainty in momentum i.e., Δp will be large, and vice versa.

Heisenberg uncertainty principle is negligible is case of large objects. (Macroscopic objects)

Explanation in terms of Compton Effect

This principal can be understood in terms of Compton Effect.

An electron is a very small particle. Therefore, to locate its position light having wavelength shorter than its size is used. (e.g. X-rays)

However, according to de-broglie equation.

$$\lambda = h / mv$$

i.e.; Photon with shorter wavelength will have high momentum. When such photon strikes an electron, it pushes the electron and disturbs its momentum. This is called Compton Effect. Thus, while determining the position of electron; we will become uncertain about the momentum of electron. If we use light of longer wavelength then determination of the position of electron becomes impossible.

Hence we cannot determine both position & momentum of electron simultaneously.

Comparison with Bohr's Theory

Bohr, in his theory, assumed that electrons are material particles and revolve around the nucleus in some definite orbits. Thus, their momentum and position can be determined with accuracy. But with the idea of wave nature of electron Heisenberg says that it can not be done.

Exercise Q14. (a):

Briefly discuss the wave mechanical model of atom. how has it given the idea of orbital. Compare orbit and orbital. *(Rawalpindi Board, 2012)*

Orbital

The volume of space in which chance of finding an electron is maximum (95%) is called orbital.

Explanation: Wave Mechanical Model of Atom

- Heisenberg uncertainty principle says that it is impossible to determine simultaneously and precisely, both position and momentum of a small fast moving particle e.g. electron.
- To overcome this problem, Schrödinger, Dirac and Heisenberg proposed wave mechanical model of atom. The best theory is that of Schrödinger.

- According to Schrödinger theory, electron is considered as a standing wave and it does not occupy a definite position in space. Schrödinger gave a wave equation, which gives probability of finding electrons in various regions in an atom. These regions are called orbitals.

Figure: Probable electron density diagram for H-atom

Example: For H-atom, the maximum probability of finding electron is at a distance of 0.053 nm from the nucleus.

This is the same distance as calculated by Bohr for the 1st orbit of H-atom.

Hence, for a distance shorter or longer than 0.053 nm, probability of finding electron decreases sharply in a hydrogen atom.

The orbital is actually a spread of charge around the nucleus. It is often called electron cloud.

	Orbit		Orbital
1	It is the circular path on which electron revolves around the nucleus.	1	It is the region in space in which probability of finding electron is maximum (about 95%)
2	This term is used in the Bohr's theory of atomic structure.	2	This term is used in quantum mechanical model.
3	It is two dimensional	3	It is three dimensional
4	Number of electrons in an orbit is given by the formula, $2n^2$. Where 'n' is the number of orbit.	4	Each orbital contains maximum two electrons.
5	In this exact position of electron is indicated.	5	Only probability of electron is given in an orbital.

Exercise Q14. (b):

What are quantum numbers? Discuss their significance.

QUANTUM NUMBERS

The behaviour of electrons in space around the nucleus is described by a set of four numbers called quantum numbers.

Quantum numbers are sets of numerical values which give acceptable solutions to Schrödinger equation for hydrogen atom.

Three quantum numbers are obtained by solving Schrödinger wave equation while spin quantum number is due to the two different orientations of electron in a magnetic field. i.e., clockwise & anticlockwise.

Four quantum numbers are

(1) Principal Quantum Number (n)

It gives information about Shells.

- It shows the approximate distance of electron from the nucleus of an atom.
- It is denoted by "n". Its value are: n = 1, 2, 3 ....
- Value of "n" tells about the energy and distance of electron from the nucleus.

  Greater the value of n, greater will be the energy and distance of electron from the nucleus & vice versa. It is the measure of size of electronic shell.
- The value of n corresponds to a definite shell e.g.
- The electrons in a shell can be determined by the formula $2n^2$

n	Shell	Capacity ($2n^2$)
1	K	$2 \times 1^2 = 2$
2	L	$2 \times 2^2 = 8$
3	M	$2 \times 3^2 = 18$
4	N	$2 \times 4^2 = 32$

(2) Azimuthal Quantum Number (ℓ)

It gives information about Sub-shells

Origin of Azimuthal Quantum Number

- A spectrometer of high resolving power shows that an individual line in a line spectrum of an atom is actually further divided into several fine lines. It means than an individual shell is further divided into several sub-shells.

  These sub-shells are explained in terms of azimuthal quantum number.
- Azimuthal quantum number is denoted by "ℓ"
- It has value from 0, 1, 2, 3 ... (n – 1).
- The numbers 0, 1, 2, 3 ... corresponds for various subshells

Examples:

0 stands for s-subshell means 'sharp'
1 stands for p- subshell means 'principle'
2 stands for d- subshell means 'diffused'
3 stands for f- subshell means 'fundamental'

These terms are used to describe the series of lines in the spectrum.

Number of Electrons in a Sub-Shell

It describes the shape of a subshell in which the electron is present.

Maximum number of electrons in a subshell can be obtained by using the formula

$2(2\ell + 1)$

Thus for

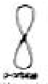
$\ell = 0$ s- subshell $2(2 \times 0 + 1) = 2$ electrons

$\ell = 1$ p- subshell $2(2 \times 1 + 1) = 6$ electrons

$\ell = 2$ d- subshell $2(2 \times 2 + 1) = 10$ electrons

$\ell = 3$ f- subshell $2(2 \times 3 + 1) = 14$ electrons

s-orbital (spherical)



p-orbital (dumbbell)

d-orbital (sausage)

Shape of Sub-Shells

Value of "ℓ" also tells about the shape of orbital

A brief summary is given below

"ℓ"	Subshell	Shape	Maximum number of Electrons
0	s	spherical	2
1	p	dumbbell	6
2	d	sausage	10
3	f	complex	14

Relationship between Principal and Azimuthal Quantum No.

The relationship is as follows

n Shell	ℓ	Subshell
1 K	0	s (1s)
2 L	0	s (2s)
	1	p (2p)
3 M	0	s (3s)
	1	p (3p)
	2	d (3d)
4 N	0	s (4s)
	1	p (4p)
	2	d (4d)
	3	f (4f) etc.
	4	

(3) Magnetic Quantum Number (m)

It gives information about the different orientation of orbitals in space.

Origin of Magnetic Quantum Number

- In the presence of magnetic field, lines in the line spectrum of an atom are further split up into various very fine lines. The appearance of these lines is explained by magnetic quantum number.
- It is represented by 'm'.
- It gives the orientation and degeneracy of the orbital is space. Hence, it is also called orbital orientation quantum number.
- It has value from $m = -\ell \ldots 0 \ldots +\ell$ or $m = 0, \pm\ell, \ldots$
- The value of 'm' shows the different ways in which a particular orbital can be arranged in space. e.g.

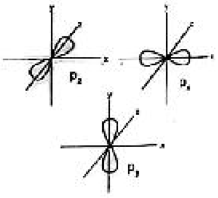
Examples:

(i) When $\ell = 0$, s-subshell, m=0

It shows that s-orbital can be arranged in space only in one way. Thus, it is not further sub-divided into other orbitals. It is a spherical and symmetrical orbital. In this probability of finding electron is same in all directions.

(ii) When $\ell = 1$, p-subshell, $m = -1, 0, +1$

It means that p-orbital have three possible orientations in space. Thus, p-orbital is further sub-divided into three orbitals along X, Y and Z-axis. These are written as p_x, p_y, p_z. These three orbitals are present perpendicular to each other.



In the absence of magnetic field all the three p-orbitals have same energy. These are called 3-fold degenerate or triply degenerate orbitals.

(iii) When $\ell = 2$, d-subshell, m= −2, −1, 0, +1, +2

Thus, d-subshell is 5-fold degenerate.

(iv) When $\ell = 2$, d-subshell, m= −3, −2, −1, 0, +1, +2, +3

Thus, f-subshell is 7-fold degenerate etc.

Formula for number of possible orientation of orbitals

For a given value of 'ℓ', the total values of 'm' are $(2\ell + 1)$

Thus for $\ell = 0$ s- subshell $(2 \times 0 + 1) = 1$ orientation

$\ell = 1$ p- subshell $(2 \times 1 + 1) = 3$ orientation

$\ell = 2$ d- subshell $(2 \times 2 + 1) = 5$ orientation

$\ell = 3$ f- subshell $(2 \times 3 + 1) = 7$ orientation

Relationship between Principal, Azimuthal and Magnetic Quantum Nos.

The relationship is given below

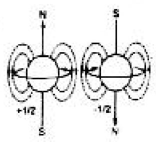
n	ℓ	m		
1	0	0	1s	
2	0	0	2s	
	1	−1	$2p_x$	Three Possible Orientations of orbitals
		0	$2p_y$	
		+1	$2p_z$	
3	0	0	3s	
	1	−1	$3p_x$	Three Possible Orientations of p-orbitals
		0	$3p_y$	
		+1	$3p_z$	
	2	−2	$3d_{xy}$	Five Possible Orientations of d-orbitals
		−1	$3d_{yz}$	
		0	$3d_{z^2}$	
		+1	$3d_{xz}$	
		+2	$3d_{x^2-y^2}$	

Spin Quantum Number(s)

It describes the spin of electron is an atom. It is denoted by s.

Origin of Spin Quantum Number

- Alkali metals have one electron in their valence shell. When this electron jumps from the excited state to the ground state, it emits light and forms a line spectrum. High resolving spectrometer shows that each line in the line emission spectrum consists of two lines. This is called doublet structure. This doublet structure is different from the fine line structure, which is explained by azimuthal quantum number.
- The lines explained by azimuthal quantum number are closely spaced, while in doublet structure two lines are widely spaced.



- In 1925, Goudsmit and Uhlenbeck suggested, that an electron also revolve about its axis. This is called self-rotation. It may be clockwise or anticlockwise. So an electron generates two opposite magnetic fields due to two opposite spins. This spin motion produces doublet line structure in the emission spectrum of an atom. It can be explained by spin quantum number.
- The spin quantum number of an electron may be + ½ or − ½

Table 5.[illegible] Quantum numbers of electrons						
[illegible]		Azimuthal Quantum number 'l'		Magnetic Quantum number 'm'	Spin Quantum number 's'	Number of electrons accommodated
1	K	0	s	0	$+\frac{1}{2}$ $-\frac{1}{2}$	2
2	L	0 1	s p	0 +1, 0, -1	$+\frac{1}{2}$ $-\frac{1}{2}$ $+\frac{1}{2}$ $-\frac{1}{2}$	2 6 } 8
3	M	0 1 2	s p d	0 +1, 0, -1 +2, +1, 0, -1, -2	$+\frac{1}{2}$ $-\frac{1}{2}$ $+\frac{1}{2}$ $-\frac{1}{2}$ $+\frac{1}{2}$ $-\frac{1}{2}$	2 6 } 18 10
4	N	0 1 2 3	s p d f	0 +1, 0, -1 +2, +1, 0, -1, -2 +3, +2, +1, 0, -1, -2, -3	$+\frac{1}{2}$ $-\frac{1}{2}$ $+\frac{1}{2}$ $-\frac{1}{2}$ $+\frac{1}{2}$ $-\frac{1}{2}$ $+\frac{1}{2}$ $-\frac{1}{2}$	2 6 10 } 32 14

Exercise Q14: Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

SHAPES OF ORBITALS

The shapes of orbitals can be explained on the basis of azimuthal and magnetic quantum number.

Consider the shapes of s, p and d-orbitals.

Shape of s-Orbital

There is only one value of magnetic quantum number for s-orbital. Thus it has only one orbital.

s-orbital is spherical in shape. It is represented by a circle as shown in figure.

Size of s-orbitals increase with increase in the value of principal quantum number (n). Thus 2s orbital is larger in size than 1s orbital and 3s orbital is larger in size than 2s orbital.

The probability of finding electron is zero between two orbitals. This region is called nodal plane or nodal surface.

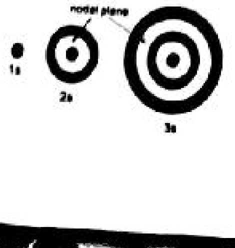


Figure: [illegible]

Shape of p-Orbital

There are three values of magnetic quantum number for p-subshell. Thus, it has three orientations in space along three axes X, Y and Z.

These three orbitals are written as p_x, p_y and p_z as shown in figure. These three orbitals are present perpendicular to each other.

p-orbital has directional nature. Thus it gives definite shape to molecules.

All the p-orbitals have similar shapes.

But the size of p-orbital increases with increase in value of principal quantum number (n).

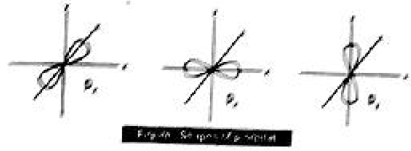


Figure: Shapes of p-orbital

Shapes of d-Orbitals

There are five values of magnetic quantum number for d-orbital. Thus it has five orientations in space.

These five orbitals are written as d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$ and d_{z^2}.

All the five orbitals do not have same shape. d_{xy}, d_{xz}, d_{yz} and $d_{x^2-y^2}$ have four lobes each, while d_{z^2} have only two lobes and a doughnut at the centre.

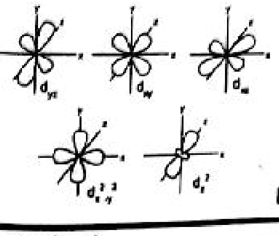


Figure: Shapes of d-orbitals

Shape of f-orbitals is very complicated

Exercise Q15. (a):

Discuss rules for the distribution of electrons in energy sub-levels and in orbitals.

ELECTRONIC DISTRIBUTIONS

1. An orbital like s, p_x, p_y, p_z and d_{xy} etc. can have maximum two electrons.
2. The maximum number of electrons in a shell is calculated by the formula $2n^2$, where 'n' is the orbit number.

There are some rules for the distribution of electrons in different sub-shells.

(1) Aufbau Principle

According to Aufbau (German word, Building up) principle

Electrons are filled in subshells in order of increasing energy values.

- The energy of orbital is determined from the $(n+\ell)$ rule.
- Lower the $(n+\ell)$ value lower will be the energy of orbital & vice versa.
- If two orbital have same $(n+\ell)$ value then lower the value of n lower will be the energy of orbital & vice versa.

Examples

Orbital	$(n+\ell)$ value	n value	Remarks
4s	4+0=4	4	Thus, 4s is of
3d	3+2=5	3	lower energy
4p	4+1=5	4	Thus, 3d is of
3d	3+2=5	3	lower energy

Table 5.4 Arrangement of orbitals according to n+l rule

	n	l	n+l
1s	1	0	1+0=1
2s	2	0	2+0=2
2p	2	1	2+1=3
3s	3	0	3+0=3
3p	3	1	3+1=4
3d	3	2	3+2=5
4s	4	0	4+0=4
4p	4	1	4+1=5
4d	4	2	4+2=6
4f	4	3	4+3=7
5s	5	0	5+0=5
5p	5	1	5+1=6
5d	5	2	5+2=7
5f	5	3	5+3=8
6s	6	0	6+0=6
6p	6	1	6+1=7
6d	6	2	6+2=8
6f	6	3	6+3=9
7s	7	0	7+0=7

Thus on the basis of this rule, order of filling of orbitals will be

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p...

2. Pauli's Exclusion Principle

According to this principle

It is impossible for two electrons residing in the same orbital of a poly-electron atom to have the same values of four quantum numbers.

or

Two electrons in the same orbital should have opposite spin (↓↑)

Example

Consider 1s orbital.

For a single electron in this orbital

n=1 ℓ=0 m=0 & let s = +1/2 indicated by ↿

Another electron enters in this orbital only if it has opposite spin to that of first.

Thus for this second electron

n=1 ℓ=0 m=0 & s = −1/2 indicated by ⇂

Thus two electrons in an orbital will have opposite spin indicated by and their one quantum number i.e.; spin quantum number will be different.

The arrangements ⥮ and ⥯ are not possible.

Orbital containing two electrons with opposite spin is called completely filled orbital and electrons are said to be paired.

Orbital containing one electron is called half-filled orbital & electron is said to be unpaired.

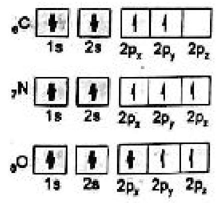
3. Hund's Rule

According to this rule

If orbitals of same energy are available, then electrons will go in separate orbitals with same spin, rather than in same orbital with opposite spin.

In other words, electrons are distributed in an atom in such a way to give maximum number of unpaired electrons.

Examples:



Electronic Configuration of Elements

Table 5.5 Electronic configuration of elements

	Atomic number	Electron Configuration Notation
Hydrogen	1	$1s^1$
Helium	2	$1s^2$
Lithium	3	$1s^2\ 2s^1$
Beryllium	4	$1s^2\ 2s^2$
Boron	5	$1s^2\ 2s^2\ 2p^1_x, 2p^0_y, 2p^0_z$
Carbon	6	$1s^2\ 2s^2\ 2p^1_x, 2p^1_y, 2p^0_z$
Nitrogen	7	$1s^2\ 2s^2\ 2p^1_x, 2p^1_y, 2p^1_z$
Oxygen	8	$1s^2\ 2s^2\ 2p^2_x, 2p^1_y, 2p^1_z$
Fluorine	9	$1s^2\ 2s^2\ 2p^2_x, 2p^2_y, 2p^1_z$
Neon	10	$1s^2\ 2s^2\ 2p^2_x, 2p^2_y, 2p^2_z$
Sodium	11	$[Ne]\ 3s^1$
magnesium	12	$[Ne]\ 3s^2$
Aluminum	13	$[Ne]\ 3s^2\ 3p^1_x, 3p^0_y, 3p^0_z$
Silicon	14	$[Ne]\ 3s^2\ 3p^1_x, 3p^1_y, 3p^0_z$
Phosphorus	15	$[Ne]\ 3s^2\ 3p^1_x, 3p^1_y, 3p^1_z$
Sulphur	16	$[Ne]\ 3s^2\ 3p^2_x, 3p^1_y, 3p^1_z$
Chlorine	17	$[Ne]\ 3s^2\ 3p^2_x, 3p^2_y, 3p^1_z$
Argon	18	$[Ne]\ 3s^2\ 3p^2_x, 3p^2_y, 3p^2_z$
Potassium	19	$[Ar]\ 4s^1$
Calcium	20	$[Ar]\ 4s^2$
Scandium	21	$[Ar]\ 4s^2\ 3d^1_{xy}, 3d^0_{yz}, 3d^0_{xz}, 3d^0_{x^2-y^2}\ 3d^0_{z^2}$
Titanium	22	$[Ar]\ 4s^2\ 3d^1_{xy}, 3d^1_{yz}, 3d^0_{xz}, 3d^0_{x^2-y^2}\ 3d^0_{z^2}$
Vanadium	23	$[Ar]\ 4s^2\ 3d^1_{xy}, 3d^1_{yz}, 3d^1_{xz}, 3d^0_{x^2-y^2}\ 3d^0_{z^2}$
Chromium	24	$[Ar]\ 4s^1\ 3d^1_{xy}, 3d^1_{yz}, 3d^1_{xz}, 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
Manganese	25	$[Ar]\ 4s^2\ 3d^1_{xy}, 3d^1_{yz}, 3d^1_{xz}, 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
Iron	26	$[Ar]\ 4s^2\ 3d^2_{xy}, 3d^1_{yz}, 3d^1_{xz}, 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
Cobalt	27	$[Ar]\ 4s^2\ 3d^2_{xy}, 3d^2_{yz}, 3d^1_{xz}, 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
Nickel	28	$[Ar]\ 4s^2\ 3d^2_{xy}, 3d^2_{yz}, 3d^2_{xz}, 3d^1_{x^2-y^2}\ 3d^1_{z^2}$
Copper	29	$[Ar]\ 4s^1\ 3d^2_{xy}, 3d^2_{yz}, 3d^2_{xz}, 3d^2_{x^2-y^2}\ 3d^2_{z^2}$
Zinc	30	$[Ar]\ 4s^2\ 3d^2_{xy}, 3d^2_{yz}, 3d^2_{xz}, 3d^2_{x^2-y^2}\ 3d^2_{z^2}$
Gallium	31	$[Ar]\ 4s^2\ 3d^{10}\ 4p^1_x, 4p^0_y, 4p^0_z$
Germenium	32	$[Ar]\ 4s^2\ 3d^{10}\ 4p^1_x, 4p^1_y, 4p^0_z$
Arsenic	33	$[Ar]\ 4s^2\ 3d^{10}\ 4p^1_x, 4p^1_y, 4p^1_z$
Selenium	34	$[Ar]\ 4s^2\ 3d^{10}\ 4p^2_x, 4p^1_y, 4p^1_z$
Bromine	35	$[Ar]\ 4s^2\ 3d^{10}\ 4p^2_x, 4p^2_y, 4p^1_z$
Krypton	36	$[Ar]\ 4s^2\ 3d^{10}\ 4p^2_x, 4p^2_y, 4p^2_z$

OBJECTIVE AND SHORT ANSWER QUESTIONS (Exercise)

Q1. Select the most suitable answer for the given questions.

(i) **The nature of positive rays depends on** *(Lahore board, 2013)*
(a) the nature of electrode
(b) the nature of the discharge tube
(c) the nature of the residual gas
(d) all of the above

(ii) **The velocity of photon is**
(a) Independent of its wavelength
(b) Depends on its wavelength
(c) Equal to square of its amplitude
(d) Depends on its amplitude

(Faisalabad Board, 2009) (D.G. Khan Board, 2012) (Multan Board, 2011)

(iii) **The wave number of the light emitted by a certain source is 2×10^6 m. The wavelength of this light will be**
(a) 500 nm (b) 500m (c) 200nm (d) 5×10^7 m

(D.G. Khan Board, 2009) (Rawalpindi board, 2011) (Gujranwala board, 2012)

(iv) **Rutherford's model of atom failed because** *(Multan Board, 2012)*
(a) the atom did not have a nucleus and electron
(b) it did not account for the attraction between proton and neutrons
(c) it did not account for the stability of the atom
(d) there is actually no space between the nucleus and the electrons

(v) **Bohr's model of atom is contradicted by** *(Multan Board, 2008)*
(a) Planck quantum theory (b) Pauli's exclusion principle
(c) Heisenberg's uncertainty principle (d) All of the above

(vi) **Splitting of spectral lines when atoms are subjected to strong electric field is called.**
(a) Zeeman effect (b) Stark effect
(c) Photoelectric effect (d) Compton effect

(Faisalabad Board, 2007) (Gujranwala Board, 2009) (Bahawalpur Board, 2010) (Rawalpindi board, 2011) (Gujranwala board, 2013) (Rawalpindi board, 2012) (Gujranwala board, 2010) 2012 (Sargodha Board, 2014)

(vii) **In the ground state of an atom, the electron is present**
(a) in the nucleus (b) in the second shell
(c) nearest to the nucleus (d) farthest from the nucleus

(Bahawalpur Board, 2009) (D.G. Khan Board, 2012) (Gujranwala board, 2013, 2014)

(viii) **Quantum number values for 2p orbitals are**
(a) $n = 2, l = 1$ (b) $n = 1, l = 2$
(c) $n = 1, l = 0$ (d) $n = 2, l = 0$

(Faisalabad Board, 2008) (Multan Board, 2010) 2013) (Sargodha Board, 2011, 2012) (Gujranwala board, 2010) (Lahore board, 2013)

(ix) Orbitals having same energy are called

(a) hybrid orbitals (b) valence orbitals
(c) degenerate orbitals (d) d-orbitals

(Faisalabad Board, 2008) (Bahawalpur Board, 2009) (Sargodha Board, 2009, 2012) (Rawalpindi Board, 2009) (Multan Board, 2010) (Faisalabad Board, 2011) (D.G. Khan Board, 2012) (D.G. Khan Board, 2012)

(x) When 6d orbital is complete, the entering electron goes into

(a) 7f (b) 7s (c) 7p (d) 7d

(Lahore Board, 2007) (Sargodha Board, 2009) (Rawalpindi Board, 2010, 2012) (Gujranwala board, 2012) (Multan Board, 2011) (Gujranwala board, 2014)

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c)

Positive rays are produced due to ionization of gases present in the discharge tube.
e.g. consider the ionization of He and Ne

$He + e^- \longrightarrow He^+ + 2e^-$
(positive ray)

$Ne + e^- \longrightarrow Ne^+ + 2e^-$
(positive ray)

Since different gases have different nature of nuclei. Therefore, nature of positive rays is different for different gases.

(ii) Ans: (a)

Light travels in the form of photons. Since velocity of light is a constant quantity, therefore, velocity is photon is also constant.

(iii) Ans: (a)

Wave length of light is given by

$\lambda = \frac{1}{\bar{v}}$, since $\bar{v} = 2 \times 10^6\ m^{-1}$, therefore

$\lambda = \frac{1}{2 \times 10^6} = 0.5 \times 10^{-6} m = 500 \times 10^{-9} m$

$= 500\ nm$

Since $1\ nm = 10^{-9} m$

(iv) Ans: (c)

According to Rutherford's atomic model, a revolving electron must emit energy continuously. As a result, electron will move in a spiral path and will fall into the nucleus. Therefore, whole atom would collapse. Hence, Rutherford's model does not account for the stability of atom.

(v) Ans: (c)

Bohr's model indicates the exact position and momentum of electron. However, according to Heisenberg uncertainty principle, both position and momentum of electron cannot be determined simultaneously. Hence, these two are opposite (contradicted) to each other.

(vi) Ans: (b)

When emission spectrum of excited H-atom is taken in an electrical field, lines are split up into component lines. This is called stark effect

(vii) Ans: (c)

In the ground state of an atom, the electron will be present at the lowest energy level. This lowest energy level will be nearest to the nucleus.

(viii) Ans: (a)

For 2p orbital, 2 stands for principle quantum number. Hence, for 2p orbital, n=2.
According to Azimuthal quantum number, when n=2, l=0,1. Here '0' stands for 's-orbital' and '1' stands for 'p' orbital. Hence, fro 2p orbital, l=1
Thus, for 2p orbital, n=2, l=1

(ix) Ans: (c)

Orbitals having same energy are called degenerate orbitals.

(x) Ans: (c)

According to (n+ℓ) rule, orbitals are filled energy wise. Thus orbitals are filled in following order
1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f, 6d, 7p...
Hence, when 6d orbital is complete, the entering electron will goes into 7p orbital.

Q2. Fill in the blanks with suitable words

(i) β-particles are nothing but ______ moving with a very high speed.
(ii) The charge on one mole of electrons is ______ coulombs.
(iii) The mass of hydrogen atom is ______ grams.
(iv) The mass of one mole of electrons is ______ grams.
(v) Energy is ______ when electron jumps from higher to a lower orbit.
(vi) The ionization energy of hydrogen atom can be calculated from ______ model of atom.
(vii) For d sub-shell, the azimuthal quantum number has ____ value.
(viii) The number of electrons in a given subshell is given by formula ______.
(ix) The electronic configuration of H^- is ______.

Answers:
(i) electrons (ii) 96500 (iii) 1.66×10^{-24} (iv) 5.48×10^{-4}
(v) released (vi) Bohr's (vii) two (viii) 2(2ℓ+1)
(ix) $1s^2$

Q3. Indicate true or false as the case may be

(i) A neutron is a slightly lighter particles than a proton.
(ii) A photon is the massless bundle of energy but has momentum.
(iii) The unit of Rydberg constant is the reciprocal of unit of length.
(iv) The actual isotopic mass is a whole number.
(v) Heisenberg's uncertainty principle is applicable to macroscopic bodies.
(vi) The nodal plane in an orbital is the plane of zero electron density.
(vii) The number of orbitals present in a sub-level is given by the formula (2ℓ + 1).
(viii) The magnetic quantum number was introduced to explain Zeemann and Stark effects.
(ix) Spin quantum number tells us the direction of spin of electron around the nucleus.

Answers:
(i) False (ii) True (iii) True (iv) False (v) False (vi) True
(vii) True (viii) True (ix) False

Q4. Keeping in mind the discharge tube experiment, answer the following questions.

(a) Why is it necessary to decrease the pressure in the discharge tube to get the cathode rays? *(Faisalabad Board, 2007: Sargodha Board, 2010: Gujranwala Board, 2012)*

OR *Gases do not conduct electricity at normal pressure. Why?* *(D.G. Khan Board, 2007)*

At high pressure, large amount of gas is present in the discharge tube. It will cause hindrance for the movement of electrons (cathode rays). Thus, conduction of electricity is difficult.

However, at low pressure amount of gas is less; therefore, electrons (cathode rays) can move and conduct electricity easily. Hence, it is necessary to decrease the pressure in discharge tube to get the cathode rays.

(b) Whichever gas is used in the discharge tube, the nature of the cathode rays remains the same. Why? *(D.G. Khan Board, 2011: Gujranwala Board, 2013)*

OR *Cathode rays do not depend upon the nature of the gas. Discuss:* *(D.G. Khan Board, 2008, 2012)*

OR *Why cathode rays are independent of nature of gas used in the discharge tube? (D.G. Khan Board, 2009: Gujranwala Board, 2014)*

OR *Why e/m values of cathode rays is same for all gases: (Sargodha Board, 2007: Lahore Board, 2009, 2013)*

The cathode rays are actually electrons. Since electrons are present in all atoms and their nature is same. Therefore, these are considered as fundamental particle of atom. Thus, nature of cathode rays remains same, no matter which gas is used in the discharge tube.

It was proved experimentally by J.J.Thomson. He calculated e/m ratio of cathode rays by taking different gases in the discharge tube. But he always found the same e/m ratio. It shows that cathode rays obtained by different gases have same nature.

(c) Why e/m value of the cathode rays is just equal to that of electron?
(Faisalabad Board, 2007: D.G. Khan Board, 2012: Bahawalpur Board, 2010: Sargodha Board, 2009: Bahawalpur Board, 2009: Gujranwala Board, 2012)

e/m ratio of cathode rays is 1.7588×10^{11} C/Kg, which is equal to that of electron. It is because cathode rays are basically electrons.

(d) The bending of the cathode rays in the electric and magnetic fields shows that they are negatively charged.

Solved on Page 240

(e) Why positive rays are also called canal rays?
(Multan Board, 2007: Azad Kashmir Board, 2012: Gujranwala Board, 2010: Bahawalpur Board, 2008, 2010: Sargodha Board, 2010: D.G. Khan Board, 2008: Gujranwala Board, 2012)

Eugein Goldstein used a perforated cathode for the discovery of positive rays. The perforated cathode have small pores which act as small canals. Since positive rays pass through these cananls, therefore, these are also called canal rays.

(f) The e/m value of positive rays for different gases are different but those for cathode rays the e/m values is the same. *(Lahore Board, 2010: Rawalpindi Board, 2011)*

OR *Why the properties of positive rays depend upon the nature of the gas?* *(Rawalpindi Board, 2007)*

Cathode rays are electrons. Moreover, nature of electrons is same in all atoms. Thus, e/m ratio is same for different gases.

Positive rays are produced due to ionization of gases present in the discharge tube.

e.g. consider the ionization of He and Ne

$$He + e^- \longrightarrow \underset{\text{(positive ray)}}{He^+} + 2e^-$$

$$Ne + e^- \longrightarrow \underset{\text{(positive ray)}}{Ne^+} + 2e^-$$

It shows that positive rays are nuclei of gases. Different gases have different nature of nuclei. Hence, e/m ratio for different positive rays is different.

(g) The e/m value for positive rays obtained from hydrogen gas is 1836 times less than that of cathode rays. *(Lahore Board, 2007: Gujranwala Board, 2011)*

Positive rays obtained from hydrogen gas in a discharge tube consists of protons and the cathode rays consists of electrons. A proton and an electron have equal magnitude of charge but mass of a proton is 1836 times greater than that of an electron. Hence, e/m value of positive ray obtained from hydrogen gas is 1836 times less than that of cathode rays.

Q5. (a) Explain Millikan's oil drop experiment to determine the charge of an electron?

Solved on Page 245

(b) What is J.J Thomson's experiment for determining e/m value of electron?

Solved on Page 245

(c) Evaluate mass of electron from the above two experiments.

Solved on Page 247

Q6. (a) Discuss Chadwick's experiment for the discovery of neutrons.

Solved on Page 243

(b) Rutherford's atomic model is based on the scattering of α-particles from a thin gold foil. Discuss it and explain the conclusions.

Solved on Page 247

Q7. (a) Give the postulates of Bohr's atomic model. Which postulate tells us that orbits are stationary and energy is quantized?

Solved on Page 250

(b) Derive the equation for the radius of nth orbit of hydrogen atom using Bohr's model.

Solved on Page 250

(c) How does the above equation tell you that

(i) Radius is directly proportional to the square of the number of orbit.

(ii) Radius is inversely proportional to the number of protons in the nucleus.

The equation for radius of n^{th} orbit of hydrogen atom is

$$r = \frac{\varepsilon_0 n^2 h^2}{\pi m Z e^2}$$

$$\text{or} \quad r = \frac{\varepsilon_0 h^2}{\pi m e^2} \times \frac{n^2}{Z} \quad \text{or} \quad r \propto \frac{n^2}{Z}$$

Hence, this equation shows that

(i) the radius is directly proportional to the square of the number of orbit (n).

(ii) the radius is inversely proportional to the atomic number (Z) which corresponds to the number of protons in the nucleus.

(d) How do you come to know that the velocities of electrons in higher orbits are less than those in lower orbits of hydrogen atom?

According to Bohr's theory, the equation for velocity of an electron in any orbit is

$$v^2 = \frac{Ze^2}{4\pi\varepsilon_0 r\, m} \quad \text{or} \quad v^2 \propto \frac{1}{r}$$

This equation shows that square of velocity of electron is inversely proportional to the radius of orbit (r). It means electrons revolve faster in an orbit of smaller radius nearer to the nucleus. As the electron moves to higher orbits of larger radius, its velocity decreases.

(e) Justify that the distance gaps between different orbits go on increasing from the lower to the higher orbits.

According to Bohr's theory, the equation for radius of orbit is

$$r = 0.529 \times n^2$$

This equation shows that radius of the orbit is directly proportional to the square of orbit number (n). Hence, higher orbits have more radii and vice versa. It means that radius of orbits goes on increasing with increasing orbit numbers.

Examples:

For n = 1 $\quad r = 0.529 \times 1^2 = 0.529\ \text{Å}$

For n = 2 $\quad r = 0.529 \times 2^2 = 2.11\ \text{Å}$

For n = 3 $\quad r = 0.529 \times 3^2 = 4.75\ \text{Å}$

So, we have $\quad r_2 - r_1 < r_3 - r_2 \cdots$

Thus, radius of orbits goes on increasing with increasing orbit numbers.

Q8. Drive the formula for calculating the energy of an electron in nth orbit using Bohr's model. Keeping in view this formula explain the followings:

Solved on Page 253

(a) The potential energy of the bounded electron is negative.

According to Bohr's theory, Potential Energy = P.E. $= -\dfrac{Ze^2}{4\pi\varepsilon_0 r}$

The minus sign indicates that the P.E. decreases when the electron is brought from infinity to distance 'r'. At infinity, the electron is not attracted by any thing, thus P.E. is zero. At a point nearer to the nucleus, electron is attracted by nucleus, thus P.E. is less than zero i.e. negative.

(b) Total energy of the bounded electron is also negative.

According to Bohr's theory, Total Energy = $E_n = -\dfrac{mZ^2e^4}{8\varepsilon_0^2 n^2 h^2}$

The minus sign indicates that the energy decreases when the electron is brought from infinity to distance 'r'. At infinity, the electron is not attracted by any thing, thus energy is zero. At a point nearer to the nucleus, electron is attracted by nucleus, thus energy is less than zero i.e. negative.

(c) Energy of an electron is inversely proportional to n^2, but energy of higher orbits are always greater than those of the lower orbits.

According to Bohr's theory, the energy of electron in n^{th} orbit of hydrogen atom is given as

$$E_n = -\frac{1313.31}{n^2}\ \text{kJ/mol}$$

Thus, it shows

(i) The energy of an electron is inversely proportional to n^2.

(ii) The negative sign indicates the attraction between electron and nucleus. As the electron moves to higher orbits, its attraction with nucleus decreases and hence its energy increases.

Examples:

For n=1 $E_1 = -\frac{1313.31}{1^2} = -1313.31$ kJ / mol

For n=2 $E_2 = -\frac{1313.31}{2^2} = -328.32$ kJ / mol etc.

Thus, the energy 'E_2' is greater than 'E_1'

(d) The energy difference between adjacent levels goes on decreasing sharply.

According to Bohr's theory, Total Energy = $E_n = -\frac{mZ^2e^4}{8\varepsilon_0^2 n^2 h^2}$

This equation shows that the energy of an electron is inversely proportional to n^2. Hence energy difference between adjacent levels goes on decreasing sharply.

The energy differences between adjacent orbits are

$E_2 - E_1 = (-328.32) - (-1313.31) = 984.99$ kJ/mol

$E_3 - E_2 = (-145.92) - (-328.32) = 182.40$ kJ/mol

$E_4 - E_3 = (-82.08) - (-145.92) = 63.84$ kJ/mol

Thus, $E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > \ldots$

Q9. (a) Derive the following equations for hydrogen atom which are related to:
(i) Energy difference between two levels, n_1 and n_2.
(ii) Frequency of photon emitted which an electron jumps from n_2 to n_1.
(iii) Wave number of the photon when the electron jumps from n_2 to n_1.

Solved on Page 260

(b) Justify that Bohr's equation for the wave number can explain the spectral lines of Lyman, Balmer and Paschen series.

Solved on Page 262

Q10. (a) What is spectrum. Differentiate between continuous spectrum and line spectrum.

Solved on Page 258

(b) Compare line emission and line absorption spectra.

Solved on Page 259

(c) What is the origin of line spectrum?

Solved on Page 256

Q11. (a) Hydrogen atom and He^+ are monoelectronic system, but the size of He^+ is much smaller than H. Why? (Multan Board, 2009)

Both hydrogen atom and He^+ ion have one electron in their outermost shell. However, the nucleus of He^+ has greater positive charge(due to two protons) than that of hydrogen atom (due to one proton). Therefore, nucleus of He^+ attracts its electron more powerfully as compared to hydrogen. Hence, size of He^+ becomes smaller than hydrogen.

(b) Do you think that the size of Li^{+2} is even smaller than He^+? Justify with calculations.

Both He^+ and Li^{2+} ions have one electron in their outermost shell. However, the nucleus of Li^+ has greater positive charge(due to three protons) than that of He^+ ion (due to two proton). Therefore, nucleus of Li^{2+} attracts its electron more powerfully as compared to He^+. Hence, size of Li^{2+} becomes smaller than hydrogen.

Mathematical Calculations

For monoelectronic systems, Bohr's equation for radius of orbit is given by

$$r = \frac{n^2}{Z} \times a_0$$

Where

n = number of orbit Z = Atomic number &

a_0 = constant = 0.529 A°

Thus for 1^{st} orbit of Li^{2+}

n = 1 Z = 3

$$r = \frac{1^2}{3} \times 0.529 = \boxed{0.176\ \text{Å}}$$

For 1^{st} orbit of He^+ ion

n = 1 Z = 2

$$r = \frac{1^2}{2} \times 0.529 = \boxed{0.264\ \text{Å}}$$

It shows that size of Li^{2+} is smaller than He^+

Q12. (a) What are X-rays? What is their origin? How was the idea of atomic number derived from the discovery of X-rays?

Solved on Page 264

(b) How does the Bohr's model justify the Moseley's equation?

According to Bohr's theory, the frequency of emitted photon is given as

$$\nu = \frac{mZ^2e^4}{8\varepsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

or $\nu \propto Z^2$

or $\sqrt{\nu} \propto Z$

Thus, when electron jumps from higher orbit 'n_2' to lower orbit 'n_1', the square root of frequency of photon emitted is directly proportional to the atomic number of the element which is the Moseley's law i.e.,

$$\sqrt{\nu} = a(Z - b)$$

or $\sqrt{\nu} \propto Z$

Q13. Point out the defects of Bohr's model. How these defects are partially covered by dual nature of electron and Heisenberg's uncertainty principle?

Solved on Page 263

Q14. (a) Briefly discuss the wave mechanical model of atom. how has it given the idea of orbital? Compare orbit and orbital. (Rawalpindi Board, 2012)

Solved on Page 268

(b) What are quantum numbers? Discuss their significance.

Solved on Page 269

(c) When azimuthal quantum number has a value 3, than there are seven values of magnetic quantum number. Give reasons.

OR *Find the value of magnetic quantum number, m, when the azimuthal quantum number, ℓ is 3.* (Sargodha Board, 2014)

The values of magnetic quantum number (m) is related to azimuthal quantum number (ℓ) by the relation

$$m = -\ell \ldots 0 \ldots, +\ell$$

Hence

When $\ell = 3$ it is f-orbital. & $m = -3, -2, -1, 0, +1, +2, +3$

Thus m has 7 values for $\ell = 3$

These seven values show that f-orbital has seven different orientations in space.

Q15. (a) Discuss rules for the distribution of electrons in energy sub-levels and in orbitals.

Solved on Page 276

(b) What is $(n + \ell)$ rule. Arrange the orbitals according to this rule. Do you think that this rule is applicable to degenerate orbitals?

The orbitals of a subshell having same $(n+\ell)$ value are called degenerate orbitals because they have same energy. Hence, $(n+\ell)$ rule cannot be applied to degenerate orbitals. However, degenerate orbitals have different values of magnetic quantum

number(m), therefore, they can be differentiated by 'm' values. e.g. $2p_x$, $2p_y$, $2p_z$ are degenerate orbitals. Their $(n+\ell)$ are same i.e., $(2+1) = 3$ but their m values are different.

(c) Distribute electrons in orbitals of $_{57}La$, $_{29}Cu$, $_{79}Au$, $_{24}Cr$, $_{53}I$, $_{86}Rn$

$_{57}La$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^0\ 5d^1$

$_{29}Cu$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$

$_{79}Au$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^1\ 4f^{14}\ 5d^{10}$

$_{24}Cr$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

$_{53}I$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^5$

$_{86}Rn$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^{10}\ 6p^6$

Q16. Draw the shapes of s, p and d-orbitals. Justify these by keeping in view the azimuthal and magnetic quantum numbers.

Solved on Page 274

IMPORTANT FORMULAS

Energy (E), frequency (ν), wavelength (λ), wavenumber ($\bar{\nu}$) and mass interconversions:

$E = h\nu$ $\quad c = \nu\lambda$ $\quad \lambda = 1/\bar{\nu}$ $\quad E = mc^2$

Bohr's equations:

Angular momentum $= mvr = \dfrac{nh}{2\pi}$

Radius of an orbit

$$r = \frac{\varepsilon_0 h^2}{\pi m e^2} \times \frac{n^2}{Z} \quad \text{Or} \quad r = a_0 \times n^2$$

Energy of an electron

$$E_n = -\frac{mZ^2e^4}{8\varepsilon_0^2 n^2 h^2} \quad \text{Or} \quad E = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2}$$

Or $E_n = -\dfrac{1313.31}{n^2}$

Wavenumber of a photon

$$\bar{\nu} = \frac{me^4}{8\varepsilon_0^2 c h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

And $P.E. = -\dfrac{Ze^2}{4\pi\varepsilon_0 r}$

$$K.E. = \frac{Ze^2}{8\pi\varepsilon_0 r}$$

Moseley's equation

$$\sqrt{\nu} = a(Z - b)$$

de-Broglie equation

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

Constants used in equations

Permittivity of vacuum

$\varepsilon_0 = 8.84 \times 10^{-12}\ C^2J^{-1}m^{-1}$

Planck's constant

$h = 6.625 \times 10^{-34}$ Js

Charge on an electron

$e = 1.6022 \times 10^{-19}$ C

Mass of an electron

$m = 9.108 \times 10^{-31}$ kg

Velocity of light

$c = 3 \times 10^8\ ms^{-1}$

Rydberg constant

$R = \dfrac{me^4}{8\varepsilon_0^2 ch^3} = 1.09678 \times 10^7\ m^{-1}$

and $a_0 = 0.529$ Å

NUMERICAL PROBLEMS (Exercise)

Q17. (a) A photon of light with energy 10^{-19} J is emitted by a source of light. (a) Convert this energy into the wavelength, frequency and wave number of the photon in terms of meters, hertz and m^{-1} respectively.

Solution:

$E = 10^{-19}$ J
$h = 6.625 \times 10^{-34}$ Js
$c = 3 \times 10^{8}$ m/s
$\nu = ?$
$\lambda = ?$
$\bar{\nu} = ?$

Since $E = h\nu$

Or $\nu = \frac{E}{h} = \frac{10^{-19}}{6.625 \times 10^{-34}} = \boxed{1.509 \times 10^{14} s^{-1}}$

Since $\lambda = \frac{c}{\nu} = \frac{3 \times 10^{8}}{1.509 \times 10^{14}} = \boxed{1.988 \times 10^{-6} m}$

Since $\bar{\nu} = \frac{1}{\lambda} = \frac{1}{1.988 \times 10^{-6}} = \boxed{5.030 \times 10^{5} m^{-1}}$

(b) Convert this energy of the photon into ergs and calculate the wave length in cm, frequency in Hz and wave number in cm^{-1}

$h = 6.625 \times 10^{-34}$ Js $\quad c = 3 \times 10^{8}$ m/s
$E = 10^{-19}$ J $= 10^{-19} \times 10^{7} = 10^{-12}$ erg
$h = 6.625 \times 10^{-34}$ Js $= 6.625 \times 10^{-34} \times 10^{7}$ erg s $= 6.625 \times 10^{-27}$ erg s
$c = 3 \times 10^{8}$ m/s $= 3 \times 10^{10}$ cm/s
$\nu = ?$
$\lambda = ?$
$\bar{\nu} = ?$

1 J = 10^{7} erg 1m = 100 cm erg is the unit of energy in c.g.s. sytem.

$\nu = \frac{E}{h} = \frac{10^{-12}}{6.625 \times 10^{-27}} = \boxed{1.509 \times 10^{14} s^{-1}}$

$\lambda = \frac{c}{\nu} = \frac{3 \times 10^{10}}{1.509 \times 10^{14}} = \boxed{1.988 \times 10^{-4} cm}$

$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{1.988 \times 10^{-4}} = \boxed{5.030 \times 10^{3} cm^{-1}}$

Q18. The formula for calculating the energy of an electron in hydrogen atom given by Bohr's model

$$E_n = -\frac{me^4}{8\varepsilon_0^2 n^2 h^2}$$

Calculate the energy of electron in first orbit of hydrogen atom.

Solution:

$\varepsilon_0 = 8.85 \times 10^{-12}\ C^2 J^{-1} m^{-1}$
$h = 6.625 \times 10^{-34}$ Js
$m = 9.1 \times 10^{-31}$ kg
$e = 1.6022 \times 10^{-19}$ C
$E_1 = ?$
$n = 1$

Energy in the first orbit is given by

$$E_1 = -\frac{me^4}{8\varepsilon_0^2 n_1^2 h^2}$$

$$E_1 = -\frac{(9.1 \times 10^{-31})(1.602 \times 10^{-19})^4}{8 \times (8.85 \times 10^{-12})^2 \times 1^2 \times (6.625 \times 10^{-34})^2}$$

$$E_1 = \boxed{-2.18 \times 10^{-18} J}$$

Q19. Bohr's equation for the radius of nth orbit of electron in hydrogen atom is

$$r_n = \frac{\varepsilon_0 n^2 h^2}{\pi m e^2}$$

While doing calculations take care of units of energy parameter.

(a) When the electron moves from n = 1 to n = 2, how much does the radius of the orbit increases.

Solution:

$\varepsilon_0 = 8.85 \times 10^{-12}\ C^2 J^{-1} m^{-1}$
$h = 6.625 \times 10^{-34}$ Js
$m = 9.1 \times 10^{-31}$ Kg
$e = 1.6022 \times 10^{-19}$ C

Radius of nth orbit is given by

$$r_n = \frac{\varepsilon_0 h^2}{\pi m e^2} \times n^2$$

$$r_n = \frac{(8.85 \times 10^{-12} C^2 J^{-1} m^{-1})(6.625 \times 10^{-34} Js)^2}{3.14 \times (9.1 \times 10^{-31} kg)(1.602 \times 10^{-19} C)^2} \times n^2$$

$$r_n = 0.529 \times 10^{-10}\,m \times n^2 = 0.529\,Å \times n^2$$

Thus for n=1

$$r_1 = 0.529 \times 1^2 = 0.529\,Å$$

Thus for n= 2

$$r_2 = 0.529 \times 2^2 = 2.11\,Å$$

Hence increase in radius $= r_2 - r_1 = 2.11\,Å - 0.529\,Å = \boxed{1.581\,Å}$

(b) What is the distance travelled by the electron when it goes from n=2 to n=3 and n=9 to n=10?

Solution:

Since $r_n = 0.529 \times 10^{-10}\,m \times n^2 = 0.529\,Å \times n^2$ $\boxed{10^{-10}\,m = 1\,Å}$

Thus for n=2

$$r_2 = 0.529 \times 2^2 = 2.11\,Å$$

Thus for n= 3

$$r_3 = 0.529 \times 3^2 = 4.75\,Å$$

Hence distance travelled $= r_3 - r_2 = 4.75\,Å - 2.11\,Å = \boxed{2.65\,Å}$

Also for n=9

$$r_9 = 0.529 \times 9^2 = 42.849\,Å$$

And for n= 10

$$r_{10} = 0.529 \times 10^2 = 52.9\,Å$$

Hence distance travelled $= r_{10} - r_9 = 52.9\,Å - 42.849\,Å = \boxed{10.05\,Å}$

Q20. Answer the following questions, by performing the calculations.

(a) Calculate the energy of first five orbits of hydrogen atom and determine the energy difference between them.

Energy of electron in nth orbit is given by

$$E_n = -2.18 \times 10^{-18} \times \frac{Z^2}{n^2}$$

Where Z = atomic number n = number of orbit

For Hydrogen Atom Z = 1

Therefore

$$E_n = -2.18 \times 10^{-18} \times \frac{1}{n^2}$$

Thus

For n = 1 $E_1 = -2.18 \times 10^{-18} \times \frac{1}{1^2} = -2.18 \times 10^{-18}\,J$

For n = 2 $E_2 = -2.18 \times 10^{-18} \times \frac{1}{2^2} = -5.45 \times 10^{-19}\,J = -0.545 \times 10^{-18}\,J$

For n = 3 $E_3 = -2.18 \times 10^{-18} \times \frac{1}{3^2} = -2.42 \times 10^{-19}\,J = -0.242 \times 10^{-18}\,J$

For n = 4 $E_4 = -2.18 \times 10^{-18} \times \frac{1}{4^2} = -1.36 \times 10^{-19}\,J = -0.136 \times 10^{-18}\,J$

For n = 5 $E_5 = -2.18 \times 10^{-18} \times \frac{1}{5^2} = -8.72 \times 10^{-20}\,J = -0.0872 \times 10^{-18}\,J$

Energy differences will be

$E_2 - E_1 = (-0.545 \times 10^{-18}) - (-2.18 \times 10^{-18}) = 1.635 \times 10^{-18}\,J$

$E_3 - E_2 = (-0.242 \times 10^{-18}) - (-0.545 \times 10^{-18}) = 0.303 \times 10^{-18}\,J$

$E_4 - E_3 = (-0.136 \times 10^{-18}) - (-0.242 \times 10^{-18}) = 0.106 \times 10^{-18}\,J$

$E_5 - E_4 = (-0.0872 \times 10^{-18}) - (-0.136 \times 10^{-18}) = 0.0488 \times 10^{-18}\,J$

(b) Justify that energy difference between second and third orbits is approximately five times smaller that that between first and second orbits.

Energy difference between $E_2 - E_1$ and $E_3 - E_2$

The ratio of the energy difference between $E_2 - E_1$ and $E_3 - E_2$ is given by

$$\frac{E_2 - E_1}{E_3 - E_2} = \frac{1.635 \times 10^{-18}}{3.03 \times 10^{-19}} \approx 5$$

or $\frac{1}{5}(E_2 - E_1) \approx (E_3 - E_2)$

Hence, energy difference between $E_3 - E_2$ is approximately five times smaller than $E_2 - E_1$.

(c) *Calculate the energy of electron in He^+ in first five orbits and justify that the energy differences are different from those of hydrogen atom*

For He^+ ion $Z = 2$

Therefore

$$E_n = -2.18\times10^{-18}\times\frac{Z^2}{n^2} = -2.18\times10^{-18}\times\frac{2^2}{n^2}$$

Thus

For n = 1 $E_1 = -2.18\times10^{-18}\times\frac{2^2}{1^2} = -8.72\times10^{-18}\,J$

For n = 2 $E_2 = -2.18\times10^{-18}\times\frac{2^2}{2^2} = -2.18\times10^{-18}\,J$

For n = 3 $E_3 = -2.18\times10^{-18}\times\frac{2^2}{3^2} = -9.68\times10^{-19}\,J = -0.968\times10^{-18}\,J$

For n = 4 $E_4 = -2.18\times10^{-18}\times\frac{2^2}{4^2} = -5.45\times10^{-19}\,J = -0.545\times10^{-18}\,J$

For n = 5 $E_5 = -2.18\times10^{-18}\times\frac{2^2}{5^2} = -3.488\times10^{-19}\,J = -0.3488\times10^{-18}\,J$

Energy differences will be

$E_2 - E_1 = (-2.18\times10^{-18}) - (-8.72\times10^{-18}) = 6.54\times10^{-18}\,J$

$E_3 - E_2 = (-0.968\times10^{-18}) - (-2.18\times10^{-18}) = 1.21\times10^{-18}\,J$

$E_4 - E_3 = (-0.545\times10^{-18}) - (-0.968\times10^{-18}) = 0.423\times10^{-18}\,J$

$E_5 - E_4 = (-0.3488\times10^{-18}) - (-0.545\times10^{-18}) = 0.196\times10^{-18}\,J$

Hence, difference of energy between the energy levels of He^+ is different from hydrogen.

(d) *Do you think that groups of the spectral lines of He^+ are at different places than those for hydrogen atom? give reasons.*

Since energy difference between energy levels in He^+ ion is different from hydrogen, therefore spectral lines in He^+ ions spectrum will be different from that of hydrogen spectrum.

Q21. *Calculate the value of principal quantum number if an electron in hydrogen atom revolves in an orbit of energy -0.242×10^{-18} J.*

Solution:

$E = -0.242\times10^{-18}\,J$

$Z = 1$

$n = ?$

Energy of electron in nth orbit is given by

$$E_n = -2.18\times10^{-18}\times\frac{Z^2}{n^2}$$

Hence $-0.242\times10^{-18} = -2.18\times10^{-18}\times\frac{1^2}{n^2}$

or $n^2 = \frac{-2.18\times10^{-18}}{-0.242\times10^{-18}} = 9$

$n = \sqrt{9} = \boxed{3}$

Q22. *Bohr's formula for the energy levels of hydrogen atom for any system say H, He^+, Li^{2+} etc is*

$$E_n = -\frac{mZ^2e^4}{8\varepsilon_0^2n^2h^2}$$

$$E_n = -K\left(\frac{Z^2}{n^2}\right)$$

For hydrogen Z = 1 and for He^+, Z = 2.

(a) Draw an energy level diagram for hydrogen atom and He^+.

(b) Thinking that K = 2.18×10^{-18} J, calculate the energy needed to remove the electron from hydrogen atom and from He^+.

Solution:

$K = 2.18\times10^{-18}\,J$

For hydrogen Z = 1

Energy in nth orbit is given by

$$E_n = -K\left(\frac{Z^2}{n^2}\right)$$

For n = 1 $E_1 = -2.18\times10^{-18}\left(\frac{1^2}{1^2}\right) = -2.18\times10^{-18}\,J$

For n = ∞ $E_\infty = -2.18\times10^{-18}\left(\frac{1^2}{\infty^2}\right) = 0\,J$

Hence, to move an electron from hydrogen's first orbit to an infinite distance, the energy required will be

$E_\infty - E_1 = 0 - (-2.18\times10^{-18}) = \boxed{2.18\times10^{-18}\,J}$

This is the ionization energy of hydrogen atom

For He^+ ion $Z = 2$

Energy in nth orbit is given by

$$E_n = -K\left(\frac{Z^2}{n^2}\right)$$

For $n = 1$ $\quad E_n = -2.18\times10^{-18}\left(\frac{2^2}{1^2}\right) = -8.72\times10^{-18}\,J$

For $n = \infty$ $\quad E_\infty = -2.18\times10^{-18}\left(\frac{2^2}{\infty^2}\right) = 0J$

Hence to move an electron from He^+ ion's first orbit to an infinite distance, the energy required will be

$$E_\infty - E_1 = 0-(-8.72\times10^{-18}) = \boxed{8.72\times10^{-18}J}$$

This is the ionization energy of He^+ ion.

(c) How do you justify that the energies calculated in (b) are the ionization energies of H and He^+?

The amount of energy required to remove an electron from an atom or ion to an infinite distance is called ionization energy.

Hence, 2.18×10^{-18} J and 8.72×10^{-18} J are the ionization energies of H-atom and He^+ ion respectively.

(d) Use Avogadro's number to convert ionization energy values in $kJmol^{-1}$ for H and He^+.

The ionization energy of H-atom in kJ/mol is given as

$$E = 2.18\times10^{-18}\times\frac{6.02\times10^{23}}{1000} = \boxed{1312.36\ kJ/mol}$$

The ionization energy of He^+-ion in kJ/mol is given as

$$E = 8.72\times10^{-18}\times\frac{6.02\times10^{23}}{1000} = \boxed{5249.4\ kJ/mol}$$

(e) The experimental values of ionization energy of H and He^+ are 1331 kJ mol^{-1} and 5250 kJ mol^{-1} respectively. How do you compare your values with experimental values?

The calculated values of ionization energies for H-atom and He^+-ion using Bohr's theory are 1312.36 kJ/mol and 5249.4 kJ/mol respectively.

These results agree well with the experimental results i.e. 1331 kJ/mol for H-atom and 5250 kJ/mol for He^+ ion.

Both H-atom and He^+ ion consists of one electron each and the above results clearly shows that Bohr's theory is perfectly applicable to one electron system.

Q23. Calculate the wave number of the photon when the electron jumps from
(i) n = 5 to n = 2.
(ii) n = 5 to n = 1.
In which series of spectral lines these photons will appear.

Solution:

Rydberg constant = $R = 1.097 \times 10^7\,m^{-1}$

When electron jumps from $n = 5$ to $n = 2$.

The wave number of the photon is given by the eq.

$$\bar{v} = R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) = 1.097\times10^7\left(\frac{1}{2^2}-\frac{1}{5^2}\right)$$

$$\bar{v} = 1.097\times10^7\left(\frac{1}{4}-\frac{1}{25}\right)$$

$$\bar{v} = 1.097\times10^7\times\frac{21}{100} = 2.30\times10^6\,m^{-1}$$

This spectral line is present in visible region(Balmer Series)

When electron jumps from $n = 5$ to $n = 1$.

The wave number of the photon is given by the eq.

$$\bar{v} = R\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) = 1.097\times10^7\left(\frac{1}{1^2}-\frac{1}{5^2}\right)$$

$$\bar{v} = 1.097\times10^7\left(\frac{1}{1}-\frac{1}{25}\right)$$

$$\bar{v} = 1.097\times10^7\times\frac{24}{25} = \boxed{1.05\times10^7\,m^{-1}}$$

This spectral line is present in UV region (Lyman Series)

Q24. A photon of a wave number $102.70 \times 10^5\,m^{-1}$ jumps from higher to n = 1.
(a) Determine the number of that orbit from where the electron falls.

Solution:

Rydberg constant $= R = 1.097 \times 10^7\,m^{-1}$

$n_1 = 1$

$n_2 = ?$

The wave number of the photon is given by the eq.

$$\bar{v} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$102.7\times10^5 = 1.097\times10^7\times\left(\frac{1}{1^2} - \frac{1}{n_2^2}\right)$$

$$\frac{102.7\times10^5}{1.097\times10^7} = 1 - \frac{1}{n_2^2}$$

$$0.93637 = 1 - \frac{1}{n_2^2}$$

$$\frac{1}{n_2^2} = 1 - 0.93637 = 0.0636$$

or $$n_2^2 = \frac{1}{0.0636}$$

$$n_2 = \sqrt{\frac{1}{0.0636}} = \boxed{3.96 \approx 4}$$

(b) Indicate the name of the series to which this photon belongs.

This spectral line is present in Lyman series

(c) If the electron will fall from higher orbit to n = 2, then calculate the wave number of the photon emitted. Why this energy difference is so small as compare to above calculations?

When electron jumps from n = 4 to n = 2.

The wave number of the photon is given by the eq.

$$\bar{v} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 1.097\times10^7\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\bar{v} = 1.097\times10^7\left(\frac{1}{4} - \frac{1}{16}\right)$$

$$\bar{v} = 1.097\times10^7\times\frac{3}{16} = \boxed{2.05646\times10^6\ m^{-1}}$$

Energy difference for n=4 to n=1 can be calculated by the eq.

$$\Delta E = 2.18\times10^{-18}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Thus $$\Delta E = 2.18\times10^{-18}\left(\frac{1}{1^2} - \frac{1}{4^2}\right)$$

$$\Delta E = 2.18\times10^{-18}\left(\frac{1}{1} - \frac{1}{16}\right)$$

$$\Delta E = 2.18\times10^{-18}\times\frac{15}{16} = \boxed{2.04\times10^{-18} J}$$

And the energy difference for n=4 to n=2 can be calculated by the eq

Thus $$\Delta E = 2.18\times10^{-18}\left(\frac{1}{2^2} - \frac{1}{4^2}\right)$$

$$\Delta E = 2.18\times10^{-18}\left(\frac{1}{4} - \frac{1}{16}\right)$$

$$\Delta E = 2.18\times10^{-18}\times\frac{3}{16} = 4\times10^{-19} = \boxed{0.4\times10^{-18} J}$$

The energy difference in second case is small.

It is because electron travel more distance from n=4 to n=1 than n=4 to n=2. And since energy is directly related to the distance of the electron, hence energy difference in second case is smaller than first case.

Q25. (a) What is de Broglie's wavelength of an electron travelling at half a speed of light?

Solution:

Mass of electron $= m = 9.1 \times 10^{-31}$ kg

Velocity of light $= c = 3 \times 10^8$ m/s

Velocity of electron $= v = \frac{c}{2} = \frac{3\times10^8}{2} = 1.5\times10^8$ m/s

$h = 6.625 \times 10^{-34}$ J s

$\lambda = ?$

10^{-12} m = 1pm

Wavelength of the electron is given by

$$\lambda = \frac{h}{mv} = \frac{6.625\times10^{-34}}{9.1\times10^{-31}\times1.5\times10^8} = \boxed{4.85\times10^{-12} m = 4.85\ pm}$$

(b) Convert the mass of electron into grams and velocity of light into cm s^{-1}. Calculate the wavelength of an electron in cm.

Solution:

1 J = 10^7 erg
1m = 100 cm

$m = 9.1\times10^{-31}$ kg $= 9.1\times10^{-31}\times1000g = 9.1 \times 10^{-28}$g

Velocity of light $= c = 3 \times 10^8$ m/s $= 3 \times 10^{10}$ cm/s

Velocity of electron $= v = \frac{c}{2} = \frac{3\times10^{10}}{2} = 1.5\times10^{10}$ m/s

Planck's constant $= h = 6.625\times10^{-34}$ J s $= 6.625\times10^{-34}\times10^7$ erg s

$= 6.625\times10^{-27}$ erg s

$\lambda = ?$

Wavelength of the electron is given by

$$\lambda = \frac{h}{mv} = \frac{6.625\times10^{-27}}{9.1\times10^{-28}\times1.5\times10^{10}} = \boxed{4.85 \times 10^{-10}\text{ cm}}$$

(c) Convert the wave length of electron from meters to

(i) nm (ii) Å (iii) pm

$\lambda = 4.85 \times 10^{-12}$ m

Solution:

(i) 1 m = 10^{9} nm

Therefore

$\lambda = 4.85 \times 10^{-12} \times 10^{9}\text{ nm} = \boxed{4.85 \times 10^{-3}\text{ nm}}$

(ii) 1 m = 10^{10} A°

Therefore

$\lambda = 4.85 \times 10^{-12} \times 10^{10}\text{ Å} = 4.85 \times 10^{-2}\text{ Å} = \boxed{0.0485\text{ Å}}$

(iii) 1 m = 10^{12} pm

Therefore

$\lambda = 4.85 \times 10^{-12} \times 10^{12}\text{ pm} = \boxed{4.85\text{ pm}}$

HELLO! Mr. Question here!

OBJECTIVE: Multiple Choice Questions from PAST PAPERS

1. Maximum number of electrons in an orbital is: *(Lahore board, 2014)*
(a) 6 (b) 10 (c) 14 (d) 2

2. $^{59}_{29}Cu \longrightarrow ^{60}_{30}Zn + X$ where X is: *(Lahore board, 2014)*
(a) Proton (b) Position (c) Electron (d) Neutron

3. Lines of Paschen series are produced when electrons jump from higher orbits to .... Orbit. *(Gujranwala board, 2008)*
(a) 1^{st} (b) 2^{nd} (c) 3^{rd} (d) 4^{th}

4. The electronic configuration of an atom is $1s^2\ 2s^2\ 2p^4$. The number of unpaired electrons in this atom is: *(Gujranwala board, 2008)*
(a) 0 (b) 2 (c) 4 (d) 6

5. Negative charge on cathode rays was established by: *(Gujranwala board, 2009)*
(a) William Crook (b) J Perin (c) J.J. Thomson (d) Hittrof

6. The e / m value for positive rays is maximum for: *(Gujranwala board, 2009)*
(a) hydrogen (b) helim (c) oxygen (d) nitrogen

7. Bombardment of α-particles on Beryllium (Be) atom emits neutron and this process is called: *(Gujranwala board, 2011)*
(a) natural radioactivity (b) artificial radioactivity
(c) Pauli exclusion principle (d) Hund's rule

8. Balmer series in hydrogen spectrum lies in the region: *(Gujranwala board, 2011)*
(a) ultraviolet (b) visible (c) infrared (d) microwave

9. Positive rays were discovered by: *(Multan Board, 2011)*
(a) J.J. Thomson (b) Ruther ford (c) William Crooks (d) Eugene Gold Stein

10. Lyman series lies in: *(Multan Board, 2011)*
(a) UV region (b) Visible region (c) IR region (d) Microwave region

11. Cathode rays cause a chemical change because they have .... effect. *(Rawalpindi Board, 2013)*
(a) Oxidizing (b) Conducting (c) Reducing (d) Diffusing

12. After filling of 4f, the entering electron goes into: *(Multan Board, 2013)*
(a) 5d (b) 6p (c) 6s (d) 4d

13. The positive particle produced in the discharge tube from Hydrogen gas was named Proton by: *(Multan Board, 2013)*
(a) Milikan (b) Goldstein (c) Rutherford (d) Chadwick

14. An orbital which is spherical and symmetrical is: *(Lahore Board, 2009)*
    (a) s-orbital (b) p-orbital (c) d-orbital (d) f-orbital
15. Angstrom is the unit of *(Lahore Board, 2009)*
    (a) time (b) length (c) Mass (d) Frequency
16. Properties of waves are: *(Faisalabad Board, 2009)*
    (a) Wave length (b) Wave number (c) Frequency (d) all
17. The nature of anode rays depend on *(Rawalpindi Board, 2009)*
    (a) The nature of the electrode (b) The nature of the residual gas
    (c) The nature of the discharge tube (d) All of above
18. Total number of spectral regions in a spectrum is: *(Lahore Board, 2010)*
    (a) 4 (b) 6 (c) 7 (d) 8
19. The value of Plank's constant is *(Lahore Board, 2010)*
    (a) 6.62×10^{-34} J.s (b) 6.62×10^{-27} J. s
    (c) 6.62×10^{-21} J.s (d) 6.62×10^{-31} J . s
20. In discharge tube experiment the pressure of gas was measured at *(Bahawalpur Board, 2010)*
    (a) 760 torr (b) 0.1 torr (c) 0.01 torr (d) 10 torr
21. The number of neutron present in $^{39}_{19}K$ is *(Faisalabad Board, 2011)*
    (a) 39 (b) 18 (c) 20 (d) 19
22. Lyman series occur in: *(Lahore Board, 2007)*
    (a) visible region (b) U.V. region (c) I.R. region (d) None of these
23. Balmer series is found in *(Faisalabad Board, 2007)*
    (a) I.R. region (b) U.V region (c) visible region (d) None of these
24. Which equation correctly represents the Heisenberg's uncertainty principle? *(Faisalabad Board, 2010) (Sargodha Board, 2013)*
    (a) $\Delta X \times \Delta P = \frac{h}{4\pi}$ (b) $\Delta X \times \Delta P > \frac{h}{4\pi}$
    (c) $\Delta X \times \Delta P \geq \frac{h}{4\pi}$ (d) $\Delta X \times \Delta P \leq \frac{h}{4\pi}$
25. $^{63}_{29}Cu + ^{1}_{0}n \longrightarrow ^{64}_{29}Cu + "x"$. What is "X"? *(Faisalabad Board, 2010)*
    (a) electron (b) proton (c) Beta rays (d) gamma rays
26. The wavelength of Lyman series lies in the region. *(Sargodha Board, 2010)*
    (a) U.V (b) visible (c) I.R (d) None of the above
27. Number of neutrons present in $^{39}_{19}K$ is *(D.G. Khan Board, 2010)*
    (a) 20 (b) 19 (c) 39 (d) 18

28. Value of the Redberg's constant is *(D.G. Khan Board, 2010)*
    (a) $1.7904\times 10^{7}\,m^{-1}$ (b) $1.9768\times 10^{7}\,m^{-1}$
    (c) $1.09678\times 10^{7}\,m^{-1}$ (d) $1.6\times 10^{7}\,m^{-1}$
29. Mass of electron is *(Lahore Board, 2011)*
    (a) 9.1095×10^{31} kg (b) 9.1095×10^{-31} kg
    (c) 9.1095×10^{-27} kg (d) 9.1095×10^{-31} g
30. Neutron was discovered by *(Lahore Board, 2011) (Sargodha Board, 2014)*
    (a) Chadwick (b) C.D Andersen (c) Rutherford (d) Goldstein
31. When 4s orbital is complete, the electron goes into *(Sargodha Board, 2010)*
    (a) 4p orbital (b) 3d (c) 4d (d) 4f
32. The limiting line of Balmer Series lies in the region *(Sargodha Board, 2011)*
    (a) visible (b) U.V. (c) Near I.R. (d) Far I.R.
33. Lyman Series lies in spectral region *(Sargodha Board, 2013)*
    (a) Infrared (b) ultraviolet (c) visible (d) none of these

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(d)	2	(c)	3	(c)	4	(b)	5	(c)
6	(a)	7	(b)	8	(b)	9	(d)	10	(a)
11	(c)	12	(a)	13	(c)	14	(a)	15	(b)
16	(d)	17	(b)	18	(c)	19	(a)	20	(c)
21	(c)	22	(b)	23	(c)	24	(c)	25	(d)
26	(a)	27	(a)	28	(c)	29	(b)	30	(a)
31	(b)	32	(b)	33	(b)				

Detailed Explanation of Past Papers MCQs & answers to all Past Papers SHORT QUESTONS in COLLEGE CHEMISTRY OBJECTIVE BOOK-I

CAHTODE RAYS AND ITS PROPERTIES

Short Questions

(1) *How will you prove that cathode rays are material particles with negative charge? (Lahore Board, 2007; Gujranwala Board, 2008; Multan Board, 2009)*

(2) *Why cathode rays have reducing effect (or can cause chemical change)? (D.G. Khan Board, 2010; Multan Board, 2011)*

(3) How cathode rays are termed as electrons? (Faisalabad Board, 2009)

Long Questions

(1) Discuss properties of cathode rays. (Faisalabad Board, 2012)

POSITIVE RAYS AND ITS PROPERTIES

(1) Which observation tells the presence of positive rays in discharge tube? (Faisalabad Board, 2008: D.G. Khan Board, 2009)

(2) Give reason for the production of positive rays. (Lahore Board, 2013)

(3) Write properties of positive rays. (Gujranwala Board, 2011: Lahore Board, 2013)

(4) The e/m value of Positive Rays is less than Cathode Rays. Justify. (Multan Board, 2012)

(5) Explain the experiment which help us to understand the discovery of protons. (Lahore Board, 2007)

NEUTRON AND ITS PROPERTIES

Short Questions

(1) What particles are formed by the decay of free neutrons? Write balanced equation (Faisalabad Board, 2008: Sargodha Board, 2007, 2009, 2013: Lahore Board, 2014)

(2) Write down nuclear reactions involved in the conversion of Cu into Zn. (Gujranwala Board, 2014) OR How the emission of a β-particle results in the increase of atomic number of element? (Rawalpindi Board, 2013)

(3) Complete (Faisalabad Board, 2011)

(a) ${}^4_2He + {}^9_4Be \rightarrow ?$ (b) ${}^{14}_7N + {}^1_0n \rightarrow ?$

(4) How neutrons are used in the treatment of cancer? (Bahawalpur Board, 2012)

(5) Write two properties of neutron. (Gujranwala Board, 2009: Rawalpindi Board, 2009: Lahore Board, 2014):

(6) Write balanced equation for any two nuclear reactions (Multan Board, 2008: Faisalabad Board, 2013)

Long Questions

(1) Describe the discovery and Properties of neutron in Chadwick experiment. (D.G. Khan Board, 2010: Gujranwala Board, 2011: Multan Board, 2012)

(2) Discuss Chadwick's experiment for the discovery of neutron. Compare the properties with electron and proton. (Rawalpindi board 2007: Multan board 2007)

MEASUREMENT OF CHARGE TO MASS RATIO, CHARGE AND MASS OF ELECTRON

Short Questions

(1) Calculate the mass of an electron when $e/m = 1.7588 \times 10^{11}\ C\ kg^{-1}$ (Lahore Board, 2014: Faisalabad Board, 2011: Multan Board, 2011, 2013) OR How the mass of electron is calculated by using e/m value? (Multan Board, 2010: Bahawalpur Board, 2011: Lahore Board, Rawalpindi Board, 2013)

Long Questions

(1) How e/m (charge to mass ratio) value of electron was measured. (Sargodha Board, D.G. Khan Board 2012)

(2) Explain Millikan's oil drop experiment to determine the charge of an electron. (Multan Board, 2010: Gujranwala Board, 2012: Lahore Board, 2013: Lahore Board, 2013, 2014)

RUTHERFORD ATOMIC MODEL

Short Questions

(1) How did Rutherford's model of an atom first proved the existence of nucleus of the atom? (Gujranwala Board, 2008)

(2) What are the defects in Rutherford's atomic model? (Rawalpindi Board, 2009: Multan Board, 2007, 2009: Faisalabad Board, 2009, 2013: Gujranwala Board, 2013) Give two defects in Rutherford's atomic model. (Multan Board, 2008: Lahore Board, 2011: D.G. Khan Board, 2010: Sargodha Board, 2010: Rawalpindi Board, 2011: Multan Board, 2011)

Long Questions

(1) Write defects in Rutherford's model of atom. How Bohr removed them? (Sargodha Board, 2011)

PLANCK'S QUANTUM THEORY, WAVELENGTH, FREQUENCY, WAVENUMBER

Short Questions

(1) Give postulates of Planck's theory. OR What is Plank's theory (Rawalpindi Board, 2009: Lahore Board, 2013)

(2) Derive the formula for frequency of photon (only in two steps) (D.G. Khan Board, 2010)

(3) Differentiate between (or What is) frequency and wave number. (D.G. Khan Board, 2007: Multan Board, 2010: Gujranwala Board, 2011)

(4) Give the relationship between energy and frequency. (Bahawalpur Board, 2008)

(5) The energy associated with violet colour is greater than red colour in visible spectra. Why? (Lahore Board, 2007)

Long Questions

(1) (i) Write three points of Planck's quantum theory. (ii) define frequency and wavelength. (Faisalabad Board, 2010)

POSTULATES OF BOHR'S ATOMIC MODEL, RADIUS OF ORBIT

Short Questions

(1) Why the electrons move faster in an orbit of smaller radius? (Sargodha Board, 2013) OR How do you come to know that the velocities of electros in higher orbits are less than those of lower orbits.

(2) The radius of first orbit of hydrogen atom is 0.529Å. Calculate the radius of 3^{rd} orbit of hydrogen atom. (Gujranwala Board, 2013)

(3) Justify that the distance gaps between different orbits go on increasing from the lower to the higher orbits. (Faisalabad Board, 2007: Sargodha Board, 2009)

Long Questions

(1) Derive radius of revolving electron in n-th orbit of an atom. (Gujranwala Board, 2008, 2009: Faisalabad Board 2009: Bahawalpur Board 2009: Bahawalpur Board, 2010: Rawalpindi Board, 2010: Sargodha Board, 2012, 2013)

(2) Give Postulates of Bohr's atomic model. (Lahore Board, 2009: D.G. Khan Board, 2011: Multan Board, 2012: Bahawalpur Board, 2012: Gujranwala Board, 2014)

ENERGY OF ELECTRON (BOHR'S ATOMIC MODEL)

Short Questions

(1) Why potential energy of an electron (or bonded electron) is negative in an orbit of atom? (Bahawalpur Board, 2011: Sargodha Board, 2013)

(2) Total energy of bonded electron is negative. Why? **(Gujranwala Board, 2010)**

(3) The energy difference between adjacent levels in an atom goes on decreasing sharply. Why? **(Rawalpindi Board, 2007)**

(4) Calculate ionization energy of hydrogen atom by using Bohr's atomic model. **(Gujranwala Board, 2010)**

Long Questions

(1) Derive the formula for calculating the energy of an electron in nth orbit using Bohr's model. **(Faisalabad Board, 2011: Azad Kashmir Board, 2012)**

SPECTRUM

Short Questions

(1) Define spectrum. Name its two types. **(D.G. Khan Board, 2012: Multan Board, 2007, 2009: Lahore Board, 2009)** OR What is spectrum? Give one example. **(Bahawalpur Board, 2009)**

(2) Why atomic spectrum is line spectrum? **(Lahore Board, 2010)**

(3) What is atomic emission spectrum? **(Sargodha Board, 2014)** OR What is the origin of the emission of line spectrum of an atom? **(Rawalpindi Board, 2013)**

(4) What is the origin of line spectrum? **(Sargodha Board, 2009)**

(5) Differentiate between line spectrum and continuous spectrum. **(D.G. Khan Board, 2010: Lahore Board, 2014: Sargodha Board, 2011: Multan Board, 2012)**

(6) Differentiate between atomic emission and atomic absorption spectrum **(Bahawalpur Board, 2012)**

Long Questions

(1) Describe atomic emission and atomic absorption spectrum with diagram. **(Sargodha Board 2010)**

(2) What is spectrum? Differentiate between continuous and line spectrum. **(D.G. Khan board 2007)**

(3) Define Spectrum. Explain atomic emission and atomic absorption spectrum with diagram. **(Bahawalpur Board, 2011)**

EMISSION SPECTRUM OF HYDROGEN ATOM, EXPLANATION BY BOHR'S THEORY

Short Questions

(1) What is the origin of hydrogen spectrum? **(D.G. Khan Board, 2010)**

(2) Write names of spectral series of hydrogen spectrum. **(Lahore Board, 2011)**

(3) What is Lyman series? In which region it lies? **(Rawalpindi Board, 2011)**

(4) What is the origin of hydrogen spectrum on the basis of Bohr's model? **(Multan Board, 2010)**

(5) Write down the equation for energy difference of two orbits of H-atom **(Bahawalpur Board, 2010)**

DEFECTS OF BOHR'S ATOMIC MODEL

Short Questions

(1) What are the defects of Bohr's atomic model **(Gujranwala Board, 2008: Bahawalpur Board, 2008: D.G. Khan Board, 2009)** OR Give two defects of Bohr's atomic model. **(D.G. Khan Board, 2007: Multan Board, 2013: Faisalabad Board, 2012: Sargodha Board, 2011, 2014)** NOTE: For short question, two defects will be asked preferably.

(2) What is H_α line in hydrogen spectrum? Which effect explain these lines? **(D.G. Khan Board**

2010: Bahawalpur Board, 2010, 2011)

(3) Differentiate/Describe/Define Stark and Zeeman effects **(Faisalabad Board, 2011: Gujranwala Board, 2009, 2010: D.G. Khan Board, 2011: Bahawalpur Board, 2012)**

(4) State Zeeman effect OR What is Zeemann effect? **(Rawalpindi Board, 2007: Lahore Board, 2008: D.G. Khan Board, 2008: Multan Board, 2008, 2013: Sargodha Board, 2012, 2013)**

Long Questions

(1) Give defects of Bohr's Atomic Model. **(Lahore Board, 2011)** OR Describe defects in Bohr's atomic model. **(Multan Board, 2009, 2013: Lahore Board, 2014)**

X-RAYS, MOSELEY'S LAW

Short Questions

(1) What are X-rays? How they are produced? **(Sargodha Board, 2007: D.G. Khan Board, 2007: Rawalpindi Board, 2012)**

(2) How the K-series, L-series and M-series of X-rays spectrum are produced? **(Lahore Board, 2013)**

(3) What is Moseley's law? Write importance of Moseley's law **(Rawalpindi Board, 2007: D.G. Khan Board, 2010: Multan Board, 2010: Lahore Board, 2014)** OR Give importance of Moseley law **(Azad Kashmir Board, 2012: Rawalpindi Board, 2012)** OR Give the Moseley's equation. Also write its importance (or significance). **(Faisalabad Board, 2007: Lahore Board, 2009: Multan Board, 2013)**

(4) Define Moseley's law. Give its mathematical expression. **(Multan Board, 2007: Gujranwala Board, 2009: D.G. Khan Board, 2012: Faisalabad Board, 2012: Sargodha Board, 2010, 2013)** OR What is Moseley's law. **(Faisalabad Board, 2008: Lahore Board, 2011, 2012: D.G. Khan Board, 2009)**

Long Questions

(1) What are X-rays? Give the conclusions drawn by Moseley from the study of spectral lines. **(Faisalabad Board, 2013)**

DE-BROGLIE'S EQUATION, HEISENBERG'S UNCERTAINTY PRINCIPLE, ORBITAL

Short Questions

(1) Write and explain de-Broglie's equation. **(Multan Board, 2008, 2010)**

(2) Electron has its dual nature. Justify. **(Sargodha Board, 2011)**

(3) State Heisenberg's uncertainty principle and write down its mathematical form/equation/formula **(Gujranwala Board, 2009: Faisalabad Board, 2012: Multan Board, 2010, 2011, 2012: Bahawalpur Board, 2009: Lahore Board, 2009, 2013: D.G. Khan Board, 2008: Bahawalpur Board, 2011)**

(4) Explain orbital **(Lahore Board, 2010)**

DE-BROGLIE'S EQUATION, HEISENBERG'S UNCERTAINTY PRINCIPLE, ORBITAL

Short Questions

(1) What is the function of principle quantum number? **(Gujranwala Board, 2008: Faisalabad Board, 2009: Sargodha Board, 2013)**

(2) Define quantum numbers. What is the significance of Azimuthal quantum number. **(D.G. Khan Board, 2012)** OR Define Azimuthal quantum Number and give its importance. **(Sargodha Board, 2011)**

(3) State spin quantum number(s) briefly. **(Lahore Board, 2013)**

(4) Describe shapes of s and p orbitals **(Bahawalpur Board, 2009: Sargodha Board, 2007, 2014)**

Long Questions

(1) What are quantum numbers? Give the significance of any one quantum number. **(D.G. Khan Board, 2009)**

(2) What are quantum numbers? Discuss their significance? **(Faisalabad Board 2007: Sargodha board 2007)**

(3) Discuss (i) Azimuthal quantum number (ii) Magnetic quantum number **(Sargodha Board, 2013)**

(4) What are quantum numbers? Discuss Principal and Azimuthal quantum numbers **(Sargodha Board, 2014)**

(5) What are quantum numbers? Explain Principal and Magnetic quantum numbers. **(Multan Board, 2011)**

(6) Draw and explain shapes of s- and p-orbitals. **(Rawalpindi Board, 2009)**

(7) Define orbital. Discuss shapeS of its types. **(Lahore Board, 2010)**

AUFBAU PRINCIPLE, PAULI'S EXCLUSION PRINCIPLE, HUND'S RULE

Short Questions

(1) What is Aufbau principle? **(Bahawalpur Board, 2008)** OR Define and explain n+l rule **(Multan Board, 2012)** OR Why 4s sub-shell is filled first and 3d afterward. **(Sargodha Board, 2013)**

(2) State Paulis Exclusion principle with an example **(Lahore Board, 2007, 2011, 2008, 2012, 2014)**

(3) State Aufbau principle and Pauli's exclusion principle. **(Lahore Board, 2010)**

(4) Define/Describe Hund's rule. Explain with example. **(Azad Kashmir Board, 2012: D.G. Khan Board, 2010: Sargodha Board, 2012: Lahore Board, 2014: Faisalabad Board, 2013: Multan Board, 2013)**

(5) Define/ State Hund's rule and Paulis Exclusion principle **(Gujranwala Board, 2011: D.G. Khan Board, 2012: Multan Board, 2012: Rawalpindi Board, 2013)**

Long Questions

(1) Explain the following rules with examples. (i) Pauli's Exclusion principle (ii) Hund's Rule. **(D.G. Khan Board, 2012)**

ELECTRONIC CONFIGURATIONS OF ELEMENTS

Short Questions

(1) Write electronic configuration for an element with atomic number $Z = 29$ **(Faisalabad Board, 2011)**

(2) Give the electronic configuration of Ca_{20} and Br_{35} **(Faisalabad Board, 2009: D.G. Khan Board, 2011)**

(3) Distribute the electrons in Cu_{29} and Br_{35} **(Faisalabad Board, 2008: Rawalpindi Board, 2011)**

(4) Write electronic configuration of $_{19}K$ and $_{29}Cu$ OR Write electronic configuration of elements with atomic number 19 and 29 **(Lahore Board, 2008: Faisalabad Board, 2013)**

(5) Write down the electronic configuration of Fe(26) and Br(35) **(Lahore Board, 2014)**

(6) Write electronic configuration of elements with atomic number z= 24, z=37 **(Sargodha Board, 2012, 2013: Gujranwala Board, 2013)**

TEST YOUR SKILLS

Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) The wave length of Lyman Series lies in the region
(a) U.V (b) Visible (c) I.R (d) None of above

(ii) How many electrons can be accommodated in a sub-shell for which $n = 3$, $\ell = 1$?
(a) 8 (b) 6 (c) 18 (d) 32

(iii) The electronic configuration of an atom is $1s^2, 2s^2, 2p^4$. The number of unpaired electrons in this atom is
(a) 2 (b) 0 (c) 4 (d) 6

(iv) The limiting line of Balmer series lies in the region.
(a) Visible b) U.V (c) Near I.R. (d) Far I.R.

(v) Positive ions are formed from the neutral atom by the loss of
(a) Positrons (b) protons (c) electrons (d) neutrons

(vi) Cathode rays are deflected by
(a) an electric field only (b) a magnetic field only (c) by both (d) by none

(vii) e/m value for positive rays is maximum for
(a) Hydrogen (b) Helium (c) Oxygen (d) Nitrogen

(viii) Neutron possesses
(a) positive charge (b) negative charge (c) no charge (d) all are corrected

(ix) Lines of Paschen series are produced when electrons jump from higher orbits to ___ orbit
(a) 1^{st} (b) 2^{nd} (c) 3^{rd} (d) 4^{th}

(x) When atoms are volatilized, they form
(a) continuous spectrum (b) line spectrum (c) electromagnetic spectrum (d) none

(xi) In Millikan method for determination of charge on electron the air tin the chamber is ionised by
(a) Protons (b) Electron field (c) X-rays (d) α -particles

(xii) Smallest charge of electricity that has been measured so far is
(a) charge on α -particles (b) charge on electron (c) charge on X-rays (d) charge on gamma rays

(xiii) α -particles resembles
(a) He^{++} (b) He^{+} (c) He atom (d) He_2 molecule

(xiv) Splitting of spectral lines of the hydrogen atom under the influence of electric field is called
(a) Stark effect (b) Zeeman effect (c) Compton effect (d) Photoelectric effect

(xv) According to Bohr's atomic model, radius of second orbit of hydrogen atom is:
(a) 0.529 Å (b) 2.116 Å (c) 4.0 Å (d) 5.0 Å

(xvi) An orbital can heve maximum two electrons with opposite spins according to
(a) Heisenberg's principle (b) Auf bau principle (c) Hund's Rule (d) Pauli exclusion principle

(xvii) Paschan, bracket and P fund series lie in the
(a) visible region (b) Ultraviolet region (c) Microwave region (d) Infrared region

SUBJECTIVE

Time: 2:10 Hours **Marks: 68**

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write Question numbers carefully. **(22x 2)=44**

Section - I

Q2. Answer any Eight parts from the followings.

(i) Differentiate between line spectrum and continuous spectrum.

(ii) How positive rays are produced?

(iii) Define atomic orbital what is about the probability of finding electron between two orbitals?

(iv) What is the cause of origin of x-rays?

(v) e/m value of cathode rays is independent of nature of gas. Why?
(vi) State Moseley's law and write down its equation.
(vii) Write down important points of quantum theory.
(viii) Rutherford's model cannot explain the stability of atom. Why?
(ix) What is stark effect?
(x) What is the origin of line spectrum?
(xi) How X-rays are analyzed?
(xii) Calculate the energy of photon travelling with a velocity of 3×10^8 m s^{-1} and having a wavelength of 400 nm.

Q3. Answer any Eight parts from the followings.
(i) Why the pressure inside the discharge tube was reduced to 0.01 torr to produce cathode rays?
(ii) According of de Broglie's idea, only microscopic particles have the waves. Explain?
(iii) Why the positive rays were called as canal rays?
(iv) What are slow neutrons? What happens when they are bombarded on nitrogen?
(v) Why Millikan ionized air in the chamber of his apparatus to determine charge on electron?
(vi) What is the effect of magnetic field on cathode rays?
(vii) What are the results of Rutherford's α-scattering experiment?
(viii) What is an angular momentum of electron in an orbit?
(ix) Electron has its dual nature. Justify?
(x) What is (n+l) rule?
(xi) How emission spectrum of hyrogen is obtained?
(xii) What is Summerfelds modification of Bohr Atomic Model?

Q4. Answer any Six parts from the followings.
(i) Justify that the distance gaps between different orbits go on increasing from the lower to the higher orbits?
(ii) Define Azmuthal quantum Number and give its importance?
(iii) How is the wave nature of electron verified?
(iv) Heisenberg uncertainty principle is not applicable to large objects. Why?
(v) What is the concept of Schrödinger about nature of electron?
(vi) What information is obtained form azimuthal quantum number?
(vii) What are degenerate orbitals?
(viii) How is spinning motion of electron about its axis is related to the spectrum of an atom?
(ix) What is the difference between 1s, 2s and 3s orbitals?

Section – II (Attempt any three questions) (8x 3)=24

Q5. (a) Derive an expression to calculate the energy of an electron in nth orbit of H-atom. (04)
(b) How did millikan determine the charge of an electron? (04)

Q6. (a) Write a short note on Heisenberg's uncertainty principle. (04)
(b) How does spin quantum number explain the doublet structure in the spectrum of H-atom. (03)
(c) What is Zeeman effect? (01)

Q7. (a) What is Hund's rule. (02)
(b) Prove that $\lambda = \frac{h}{mv}$ (03)
(c) How will you demonstrate that cathode rays possess energy and momentum? (03)

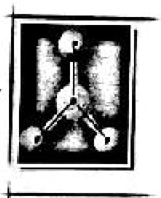
Q8. (a) Describe J.J.Thomson experiment to calculate the e/m value of electron. (03)
(b) Calculate the wave number of the photon when the electron jumps from - (03)
(i) n = 6 to n = 2. (ii) n = 6 to n = 1. In which series of spectral lines these photons will appear.
(c) Draw the shapes of d-orbitals. (02)

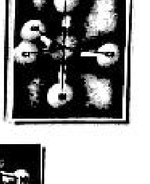
Q9. (a) Give the main points of Rutherford atomic model and also describe defects of this model. How Bohr removed these defects (03)
(b) A photon of a wave number 102.70×10^8 m^{-1} is emitted jumps from higher to n = 1. Determine the number of that orbit from where the electron falls. (03)
(c) Describe Atomic emission and Atomic Absorption spectrum with diagrams? (02)

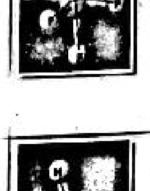
Chapter 6

CHEMICAL BONDING

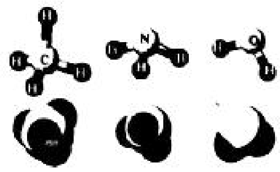
G.N. Lewis







CONTENTS



INTRODUCTION

Chemical Bond

A force that holds two or more atoms or ions together in a compound is called a chemical bond.

OCTET RULE: Cause of Chemical Combination

Octet Rule

The tendency of atoms to attain a maximum of eight electrons in the valence shell is known as octet rule.

Examples:

(I) $_{12}Mg$ ($1s^2 2s^2 2p^6 3s^2$) loses two electrons to form Mg^{+2} ion ($1s^2 2s^2 2p^6$)

(II) $_9F$ ($1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$) gain one electron to form F^{-1} ion ($1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$)

Explanation: (WHY ATOMS COMBINE TOGETHER?)

- G.N. Lewis and W. Kossel, studied the electronic configurations of elements in both free and combined state. They observed that Noble gases are highly inert. They do not react. They form only few compounds e.g. XeF_2, XeF_4, $XeOF_2$, XeO_3 etc. A noble gas does not react with another noble gas.
- It is because noble gases have eight electrons (octet) in their valence shell. Their general electronic configuration is $1s^2$ (He) or $ns^2 np^6$ (Ne, Ar, Kr, Xe, etc.)

  Examples: $_2He$ $1s^2$

  $_{10}Ne$ $1s^2 2s^2 2p^6$
- Thus, octet of noble gases is complete. Hence these are stable.
- All other elements also have tendency to stabilize themselves. An element gain stability by losing, gaining or sharing of electrons with other elements to get noble gas configuration.

NOTE:

- Many compounds do not obey octet rule.
  e.g. Formation of PCl_5, SF_6, BCl_3 etc. Hence, octet rule is not universal.
- The losing, gaining or sharing of e^- by an atom depends upon the conditions.
  e.g. In the formation of NaH, H accepts an e^- from Na.
  However, in the formation of HF, H donates major shares of its electron to the F

Energetics of Bond Formation.

According to modern theory of chemical bonding, atoms form bonds because it decreases the energy.

Example:

Consider the formation of H_2 molecule by two hydrogen atoms.

Development of Attractive and Repulsive forces

- When two atoms come close to each other, both attractive and repulsive forces are developed between them simultaneously.
- Attractive forces bring the atoms close to each other and potential energy of the system is decreased.
- Repulsive forces push the atoms away and potential energy of the system is increased.

Fig(5.1) Potential energy curve for the formation of H_2 molecules

The magnitude of potential energy for attractive forces is more than for repulsive forces. Thus, potential energy of the two hydrogen atoms decreases when they come close to each other.

Compromise Distance or Bond Distance

- In H_2 molecule, the potential energy of the system is at minimum at a distance of 75.4 pm. At this point, attractive forces dominate the repulsive forces and two hydrogen atoms are bonded to each other. Thus, it is called the bond length or bond distance or compromise distance of two hydrogen atoms.

Bond Formation Energy

At compromise distance, two hydrogen atoms are at a distance of minimum energy and these are maximum stabilized. The amount of energy released is during formation of H_2 molecule is 436.45 kJ mol^{-1}. It is called bond formation energy.

If repulsive forces dominate attractive forces, the energy of the system increases and causes instability. Thus a bond is not formed.

ATOMIC SIZES

To understand bonding, relative sizes of atoms should be known because many physical and chemical properties are related to it.

The sizes of atoms are expressed in terms of atomic radii, ionic radii, covalent radii etc. depending upon the type of compound used for its measurement.

ATOMIC RADII

The average distance between the nucleus of an atom and the outermost electronic shell while considering it spherical, is called atomic radius.

Units

The atomic radii are usually measured in picometer (pm)

$1 \text{ pm} = 10^{-12} \text{ m}$

Measurements

- Atomic radii cannot be determined directly due to following reasons.
  1. *There is no sharp boundary of an atom.* The probability of finding an electron never becomes exactly zero even at large distance from nucleus.
  2. *The electronic probability distribution is affected by neighbouring atoms.* Hence, size of an atom is changed from compound to compound.
- Atomic radii are measured from the distance between the centres of two adjacent atoms. The distance between atoms is measured with the help of X-rays or by spectroscopy.

Variation or Trend in Periodic Table

Along Period

- Atomic radii decrease along the period from left to right due to increase in positive charge on the nucleus. However, number of shells remains same along period.
- Due to increasing nuclear charge, nucleus powerfully attracts the resulting in the decrease of atomic radii. Shielding effect remains same from left to right.
- In transition elements, the decrease is small from left to right due to intervening (inner) electrons. e.g., from Sc(21) to Zn(30) and Y(39) to Cd(48).

In a Group

Atomic radii increase down the group

It is due to two factors.

(i) Increase in Number of Shells (ii) Increase in Shielding effect

(i) *Increase in Number of Shells*

In a group, number of shells increase downward. Hence, atomic radii increase.

(ii) Shielding Effect or Screening Effect

The decrease in force of attraction between outermost electrons and the nucleus due to inner shell electrons is called shielding effect.

- Down the group, numbers of shells increase. Thus, outer electrons are less attracted by nucleus due to shielding effect of inner shell electrons. These outer electrons therefore, move outward & hence atomic radii increase.
- The decrease is more in second period and less in higher periods.

IONIC RADII

The radius of the ion while considering it spherical is called ionic radius.

Units

These are generally measured in picometer ($1\ pm = 10^{-12}\ m$).

An atom may lose or gain electrons to form positive or negative ions respectively.

Ionic Radii of Positive Ion (Cation)

- An atom loses one or more electrons to form cations.
- Ionic radius of a cation is denoted by r_+.
- ***Positive ion is always smaller in size than their parent atom.***
  It is due to two reasons
  (i) In positive ion, number of electrons is reduced but positive charge on nucleus remains same. Therefore nucleus powerfully attracts outer electrons inward resulting in decrease of ionic radius.
  (ii) Sometimes, outer shell is also lost due to removal of electron, therefore, size decreases.
- ***The ionic radius of cation decreases with increase in positive charge (effective nuclear charge) on the ion.***
  Generally, greater the positive charge, smaller the size of ion and vice versa.
  It is because, due to successive loss of electrons, the nuclear charge attracts remaining electrons more powerfully and hence size is much decreased.
  Thus, the decrease in radius is larger for divalent ions e.g. Mg^{2+} and still larger for trivalent ions e.g. Al^{3+}

Examples:

Na atom = 186 pm, Na^+ ion = 95 pm
Be atom = 90 pm, Be^{2+} ion = 31 pm

Ionic Radii of Negative Ion (Anion)

- An atom gains one or more electrons to form anion.
- Ionic radius of an anion is denoted by r_-.
- ***Negative ion is always larger in size than the parent atom.***
  It is due to two reasons
  (i) Electron–electron repulsions increases due to increase in number of electrons in the valence shell. Thus ionic size increases.
  (ii) Due to increase in number of electrons, the hold of nucleus on electrons decreases. Therefore, electrons move away and thus ionic size increases.
- ***The ionic radius of negative ions increases with the increase in negative charge on the ion.***

Examples:

Cl atom = 99 pm Cl^- ion = 181 pm
O atom = 66 pm O^{2-} ion = 140 pm

Variation or Trend in Periodic Table

The variation is similar to atomic radius.

In a Group

Ionic radii increases down the group due to increase in number of shells and shielding effect.

Along Period

Ionic radii decreases from left to right due to increase in nuclear charge

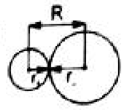
Note

Ionic radii for metals are for positive ions and for elements of group VA to VIIA are for negative ions.

Measurement

Inter-ionic Distance

The inter-ionic distance between two ions in a crystal lattice is equal to the sum of cationic and anionic radius.



Interionic distance = cationic radius + anionic radius

$$R = r_+ + r_- \quad (1)$$

Pauling determined '*R*' for KCl crystal as 314 pm. It is actually the sum of radii of K^+ and Cl^- ions

i.e. $R = r_{K^+} + r_{Cl^-}$

$R = 133 + 181 = 314$ pm

It shows that ionic radius is an additive property.

- Re-arranging equation (1), r_- of various ions in potassium salts can be determined as

$r_- = R - r_{K^+}$

- Similarly r_+ can also be determined in various chloride salts as

$r_+ = R - r_{Cl^-}$

COVALENT RADII

The covalent radius of an element is half of the single bond length between two similar atoms covalently bonded in a molecule.

Examples:

1. The bond length of H_2 molecule is 75.4 pm. So, covalent radius of H is $75.4/2 = 37.7$ pm.
2. The bond length of Cl_2 molecule is 198.8 pm. So, covalent radius of Cl is $198.8/2 = 99.4$ pm.

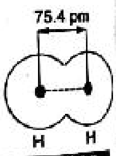


Figure: Covalent radius of H atom (75.4/2 = 37.7 pm)

Application:

The covalent radius of one atom can be used to measure the covalent radius of another atom.

Example:

Bond length of C – Cl bond in CH_3Cl is 176.7 pm. Since covalent radius of Cl is 99.4 pm, therefore covalent radius of C should be $176.7 - 99.4 = 77.3$ pm.

The variation of covalent radii in periodic table is almost similar to atomic radii

Ionization Energies, Electron Affinity and Electronegativity

Since bond formation involves energy changes, therefore, thermodynamic properties must be known to understand chemical bonding.

These properties are ionization energy, electron affinity, electronegativity etc.

IONIZATION ENERGY OR IONIZATION POTENTIAL

The ionization energy of an element is the minimum energy required to remove an electron from its gaseous atom to form an ion.

It is sometimes called as Ionization Potential.

Units

It is expressed kJ/mol or electron volts (eV)/atom

1 eV/atom $= 96.48$ kJ/mol

Example:

$Mg_{(g)} \longrightarrow Mg^+_{(g)} + e^- \quad \Delta H = +738$ kJ/mole

Factors affecting ionization energies

(i) *Atomic radius of the atom*

Increase in atomic radius decreases the ionization energy. It is because when size increases, the hold of nucleus on outer electron decreases. So, less energy is required to remove them. Hence, ionization energy decreases.

(ii) *Shielding effect of inner electrons*

Increase in atomic radius decreases the ionization energy. It is because when shielding effect increases, the hold of nucleus on outer electron decreases. So, less energy is required to remove them. Hence, ionization energy decreases.

(iii) *Nuclear charge or proton number of the atom*

Increase in nuclear charge increases the ionization energy. It is because when nuclear charge increases, the hold of nucleus on outer electron also increases. So, more energy is required to remove them. Hence, ionization energy increases.

(iv) *Nature of orbital*

The s-orbital is small and compact so it is difficult to remove electron from this orbital.

The f-orbital is larger in size, therefore, it is easy to remove electron from this orbital.

Hence, order of decreasing ionization energy is s > p > d > f

Variation or Trend In Periodic Table

In a Group

- Ionization energy decreases down the group although nuclear charge increases.
- It is due to increase in number of shells and shielding effect down the group.
- Due to addition of shells, electrons become away from nucleus and force of attraction between nucleus and outer electron decreases due to increase in distance. Shielding

effect of inner electrons also increases. Hence outer electron is easy to remove. T ionization energy decreases.

Along Period

- Ionization energy increases along the period from left to right.
- It is due to increase in nuclear charge along the period. Along period, proton num increases and thus positive charge on the nucleus increases. This high nuclear cha powerfully attracts electron. Thus, more energy is required to remove the electr therefore, ionization energies increases.
- Each period starts with an element, which has one electron in its valence shell and e with the completion of valence shell.

Higher Ionization Energies

- When first electron is removed from an atom, ionization energy is known as fi ionization energy.
- When second or third electrons are removed, these are called *Second ionization ene* or *Third ionization energy* respectively and so on.
- First, second & third ionization energy values increases in the following order.

First I.E. < Second I.E. < Third I.E.

It is because, due to removal of electron, hold of the nucleus on the remaining electro increases. Hence, they are difficult to remove and thus ionization energy increases.

Examples:

$$Mg_{(g)} \longrightarrow Mg_{(g)}^{+} + e^{-} \qquad \Delta H = +738\ kJ/mole$$

$$Mg_{(g)}^{+} \longrightarrow Mg_{(g)}^{2+} + e^{-} \qquad \Delta H = +1451\ kJ/mole$$

$$Mg_{(g)}^{2+} \longrightarrow Mg_{(g)}^{3+} + e^{-} \qquad \Delta H = +7730\ kJ/mole$$

Applications Of Ionization Energy

1. *Indication of metallic character*

   Generally

   - Elements with low ionization energies are metals
   - Elements with high ionization energies are non-metals
   - Elements with intermediate values of ionization energies are metalloids

2. *Indication of valence electrons*

   Ionization energy measurements provide evidence for the number of valence electr

   Example:

   For magnesium, the ionization energies are

   First I.E. = +738 kJ/mol, Second I. E. = +1451 kJ/mol, Third I.E. = +7730 kJ/mol

It shows, that first and second electrons are removed easily. The third electron requires much energy for removal. Since, two electrons are removed easily, so these are the valence electrons.

3. *Indication of Nature of Compounds*
   - Elements with low ionization energy values (e.g. group I A and II A), can easily give electrons, hence, they form ionic compounds.
   - Elements with intermediate ionization energies form covalent compounds by sharing electrons with other elements.

4. Stability of Atom
   - In gaseous phase, atoms and ions are isolated and have no external influences. So, ionization energy gives a quantitative measure of the stability of isolated atom.
   - Generally, higher the ionization energy, higher the stability of atoms. **e.g.**, Noble gases have highest ionization energies in their respective periods, so they are more stable.

ELECTRON AFFINITY

The electron affinity of an atom is the amount of energy released when an electron adds to an empty or partially filled orbital of an atom in its valence shell to form an anion having a unit negative charge.

Units

It is expressed as kJ/mole.

Example:

$$Cl_{(g)} + e^{-} \longrightarrow Cl^{-}_{(g)} \quad \Delta H = -349\ kJ/mole$$

Electron affinity is the measure of the attraction of the nucleus of an atom for extra electron.

Higher Electron Affinities

- During addition of first electron, energy is released, therefore, electron affinity is given negative sign.

$$O_{(g)} + e^{-} \longrightarrow O^{-}_{(g)} \quad \Delta H = -141\ kJ/mol$$

- When a second electron is added in a uni-negative ion, the incoming electron is repelled by the negative ion and energy is absorbed in the process.

$$O_{(g)}^{-} + e^{-} \longrightarrow O^{2-}_{(g)} \quad \Delta H = +844\ kJ/mol$$

- Thus first electron affinity of an atom is negative, while second, third etc. electron affinities are positive.

Measurement

Direct measurement of Electron affinity is difficult. Therefore, Electron affinities a generally measured indirectly.

Factors Affecting Electron Affinity

- Electron affinity depends upon atomic radius, nuclear charge, shielding effect etc.
- Increase in atomic radius and shielding effect decreases the attraction between nucle and incoming electron, therefore electron affinity decreases.
- Increase in nuclear charge increases the attraction between nucleus and incomin electron, so electron affinity increases.

Variation or Trend in periodic table

Along Period

- Generally, electron affinity values increase from left to right in a period due to decrea in atomic radius and increase in nuclear charge.
- Thus alkali metals on the left have lowest electron affinities and halogens on the righ have highest electron affinities.

In a Group

- Electron affinity values decrease down the group due to increase in number of shells an shielding effect.

  It is because, atomic radius and shielding effect increases down the group. Thi decreases the force of attraction between nucleus and the incoming electrons. Hence electron affinity decreases.

NOTE: Exceptions to the General Trend

- Electron affinity of F is less than Cl. It is because, F has very small size and seven electrons in 2s and 2p sub-shells. These electrons form a thick electronic cloud, which repels the incoming electron.

- The elements of group IIA, VA and VIIIA show abnormally low values in every period. It is due to two reasons
  - (i) Groups IIA and VIIIA have completely filled orbitals, therefore, incoming electrons will have to go to higher energy orbitals, resulting in the decrease of electron affinity values.
  - (ii) Group VA has half filled orbital. The repulsions between the incoming electron and the electrons present in the half filled orbital results in the decrease of electron affinity values.

ELECTRONEGATIVITY

The tendency of an atom to attract a shared electron pair towards itself in a molecule is called electronegativity.

Unit

Electronegativity has no unit.

Electronegativity Scale

- Direct measurement of electronegativity values is not possible.
- Pauling suggested an arbitrary scale from 0 to 4, as a measure of electronegativity of atoms.
- It is based upon the difference between expected bond energies of normal covalent bonds of elements and experimental bond energies.
- In this scale, electronegativity of F is arbitrarily given as 4. The electronegativities of other elements are determined relative to F.

Variations in Periodic Table

Along Period

Electronegativity values increases from left to right in a periodic table, due to decrease in atomic size and increase in nuclear charge.

In a Group

Electronegativity values decreases down the group, due to increasing number of shells and shielding effect.

In periodic table,

- the most electronegative element is Flourine (*F*)
- the least electronegative element is Francium (*Fr*).

Electronegativity and Nature of Bond

Difference of electronegativity values is an index to the polar nature of bond in a molecule.

- If electronegativity difference is zero, the bond is non-polar. Thus, all the bonds between similar atoms are non-polar. e.g., H_2
- All the bonds between different elements are generally polar e.g. HCl
- If electronegativity difference of two bonded atoms is 1.7 or greater than 1.7, bond is ionic. e.g. NaCl
- If electronegativity difference of two bonded atoms is less than 1.7, bond is covalent. e.g. HCl

TYPES OF CHEMICAL BOND

There are generally three basic types of bonds.

1. Ionic or Electrovalent bond
2. Covalent bond
3. Co-ordinate covalent bond

LEWIS CONCEPT

1. IONIC OR ELECTROVALENT BOND

The bond formed by the complete transfer of one or more electrons from an atom with low ionization energy to another atom with high electron affinity is called ionic bond.

Explanation:

- In energy terms, the electropositive elements are at higher energy state while the electronegative elements are at lower energy state. This difference of energy results in the transfer of electrons from higher energy state to lower energy state.
- The atom, which loses electron form cation, while the atom, which gains electron form anion.
- The compounds formed by the cations and anions are called ionic or electrovalent compounds.
- Generally, elements with low ionization energies (groups I-A or II-A), react with elements of high electronegativities and high electron affinities (e.g; Group VI-A or VII-A elements) to form ionic bond. e,g. NaCl, KCl etc.

Example: KCl

Formation of K^+ ion

- Electronic configuration of K is

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$$

- It can be represented as K (2, 8, 8, 1).
- K tends to loose its outermost electron and form K^+ ion. The energy required to remove one electron from K is equal to its first ionization energy.

$$K\,(2, 8, 8, 1) \longrightarrow \underset{[Ar]}{K^+\,(2, 8, 8)} + 1e^- \qquad \Delta H = 419\ kJ/mol$$

- *After loosing electron, potassium attain the nearest noble gas configuration of Ar(2, 8, 8)*

Formation of Cl^{-1} ion

- Electronic configuration of Cl atom is

$$1s^2 2s^2 2p^6 3s^2 3p^5$$

- It can be represented as Cl (2, 8, 7).

- It tends to gain one electron to attain the nearest noble gas configuration of Ar (2, 8, 8) and 349 kJ/mol energy is released. This is the electron affinity of Cl.

$$Cl\,(2, 8, 7) + 1e^- \longrightarrow \underset{[Ar]}{Cl^-\,(2, 8, 8)} \quad \Delta H = -349\ kJ/mol$$

Formation of KCl

- Thus, electron is transferred from K to Cl atom to form K^+ and Cl^- ions. These ions develop electrostatic force of attraction between them and thus ionic bonds are formed.
- K^+ and Cl^- ions arrange themselves to form crystal lattice and 690 kJ/mol energy is released. The energy released during the formation of crystal lattice is called lattice energy.

$$K^+ + Cl^- \longrightarrow KCl \qquad \Delta H = -690\ kJ/mol$$

NOTE:

- Elements of group IA (Li, Na, K, Rb, Cs) are good losers of electrons
- Elements of group VIIA(F, Cl, Br, I) are good gainers of electron.
- Thus both these combine with each other and form ionic bonds.
- Similar type of bonds are also present between elements of group IIA and group VIA elements.

Examples:

$$Ca\,(2,8,8,2) \longrightarrow Ca^{2+}\,(2,8,8) + 2e^-$$
$$Al\,(2,8,3) \longrightarrow Al^{3+}\,(2,8) + 3e^-$$
$$O\,(2,6) + 2e^- \longrightarrow O^{2-}\,(2,8)$$
$$S\,(2,8,6) + 2e^- \longrightarrow S^{2-}\,(2,8,8)$$

$$\boxed{Al^{3+}\ O^{2-} = Al_2O_3}$$

So, the formulas are

- Aluminium oxide will be Al_2O_3 (i.e., Al_2O_3 contains ions in the ratio 2:3)
- Calcium oxide will be CaO (i.e., CaO contains ions in the ratio 1:1)
- Similarly, CaS and Al_2S_3 are also ionic compounds to some extent.

Electronegativity and Nature of Compound

- Difference of electronegativity between bonded atoms can decide the nature of compound.
- Generally, If electronegativity difference is 1.7 or more, the bond is ionic. Thus, NaCl has 72% ionic character, CsF has 92% ionic character.
- Calculations show that there is no bond with 100% ionic character.

2. COVALENT BOND (ELECTRON PAIR BOND)

The bond formed by mutual sharing of electrons between two atoms is called covalent bond.

During covalent bond formation, an atom completes its valence shell by sharing and attains nearest inert gas configuration.

A covalent bond may be polar or non-polar

Non-Polar Covalent Bonds

The covalent bond, in which bonding electron pairs are equally shared by two atoms is called non-polar covalent bonds

Example

- Covalent bonds between like atoms is non-polar

H_2 and Cl_2

H : H   :Cl : Cl:

- In such compounds distribution of electron density is uniform. Due to even distribution of charge, the bonded atoms are electrically neutral. These compounds are called non-polar compounds
- CCl_4 also have equal electron density distribution. Hence it is also a non-polar compound. It is due to cancellation of all the dipoles of this molecule due to its symmetry. In CCl_4, all C–Cl bonds are polar but molecule is overall non–polar.

Other Examples:

CH_4 , SiH_4 , $SiCl_4$ etc.

Polar Covalent Bond

The covalent bond in which bonding electrons are not shared equally by atoms is called polar covalent bond

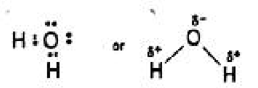
- Covalent bond between unlike atoms is polar
- In such cases, the shared electrons are more attracted by the element having larger electronegativity. It makes one end of the molecule partially positive and other end partially negative. Such compounds are called polar compounds. In these compounds distribution of electron density is not uniform

Examples

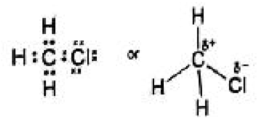
Hydrogen Flouride

H : F or $\overset{\delta+}{H}$: $\overset{\delta-}{F}$

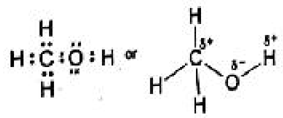
Water



Methyl Chloride



Methanol



A covalent bond can be classified as single, double or triple.

Single Covalent Bond

If covalent bond is formed by sharing of one electron pair (two electrons), it is called a single covalent bond.

Example

:Cl· + ·Cl: ⟶ :Cl : Cl: or Cl - Cl

Double Covalent Bond

If covalent bond is formed by sharing of two electron pairs (four electrons), it is called a double covalent bond.

Examples

(i) Oxygen

:O· + ·O: ⟶ :O::O: or O=O

(ii) Carbon Dioxide

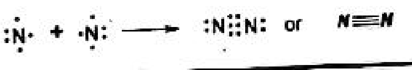
It is formed from heteroatoms. But due to linear structure polar bonds cancel the effect of each other. Hence, it is a non-polar compound.

O::C::O or O=C=O

Triple Covalent Bond

If covalent bond is formed by sharing of three electron pairs (six electrons), it is called a triple covalent bond.

Examples



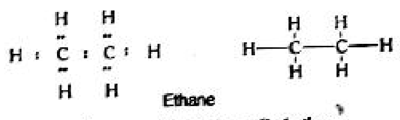
- Some non-metallic atoms especially C and Si, mutually share their electrons with each other and thus form long chain molecules called macromolecules.

  e.g. Diamond, Graphite and SiC etc.
- Carbon can form single , double or triple bonds in alkanes, alkenes and alkynes.

Alkanes

The compounds of C and H containing only single bonds are called alkanes

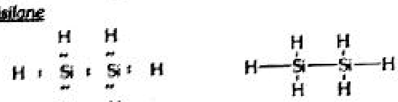
Example: Ethane



Ethane

Silicon also gives similar type of hydrides called silanes.

Example: Disilane

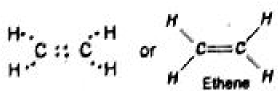


Disilane

Alkenes

The compounds of C and H containing double bonds are called alkenes

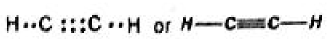
Example: Ethene



Alkynes

The compounds of C and H containing triple bonds are called alkenes

Example: Ethyne



Ethyne

3 CO-ORDINATE COVALENT BOND

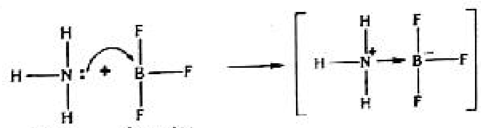
A coordinate covalent bond is formed between two atoms when the shared pair of electrons is donated by one of the bonded atoms.

- The atom which donates the electron pair is called the ' *Donor* '
- The atom which accepts them for bond formation is called the ' *Acceptor*'
- This bond is generally represented by an *arrow* pointing from donor to acceptor atom.

Examples

Reaction of Ammonia With BF_3

- A co-ordinate covalent bond is formed by the donation of electron pair form nitrogen of NH_3 to B of BF_3.
- NH_3 has three covalent bonds and one electron pair on nitrogen atom.
- In BF_3 , octet of B is not complete, therefore it is deficient in electrons.
- Thus N can donate the pair of electrons to the acceptor BF_3 and a co-ordinate covalent bond is formed.



Donor Acceptor

- The complex so formed is electrically neutral. Charges are mentioned on N and B atoms.

In some cases after bond formation, no distinction is present between a co-ordinate covalent bond and a covalent bond.

Examples

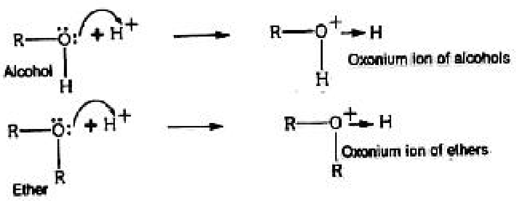
Formation of H_3O^+ Ion

When an acid is dissolved in water, a bond is formed between H_2O and H^+ ion. In this shared pair of electron is donated by O of H_2O.

All the three bonds of H_3O^+ are equal. Every bond is 33% coordinate covalent and 66% covalent.

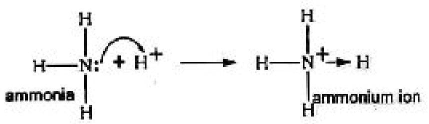
3) Formation of Oxonium Ion

Alcohols and ethers donate their lone pairs to H^+ ions to form coordinate covalent bonds. The ions produced are called oxonium ion.



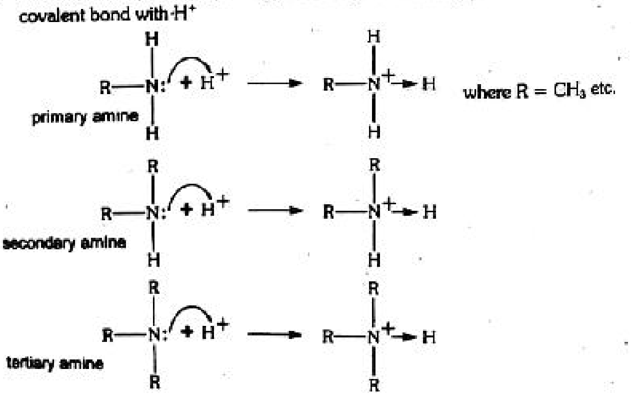
4) Formation of NH_4^+ Ion

A co-ordinate covalent bond is formed by the donation of electron to H^+ ion by nitrogen of NH_3

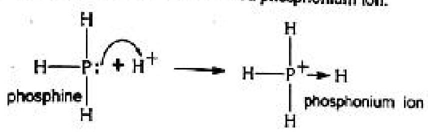


Other Examples

- Like ammonia, all the primary, secondary and tertiary amines form coordinate covalent bond with H^+



- PH_3 combines with H^+ to give PH_4^+ ion called phosphonium ion.



- Coordinate covalent bond are also present in HNO_3. Many oxyacids of halogens, like ($HClO_2$, $HClO_3$, $HClO_4$) have coordinate covalent bond between Cl and O.

Limitations of Lewis model

Lewis model has explained how the atoms are bonded to one another and how the electron pairs are shared between the bonded atoms.

Lewis model has following limitations

(i) It is an over simplified model.
(ii) It does not tell about the shapes of molecules. Many physical and chemical properties of molecules depend upon three dimensional arrangement of their atoms.
(iii) It does not tell about the bond distances, various energy transitions as shown by spectroscopic techniques.
(iv) It does not account for the unique behaviour of molecules during chemical reactions.

Qualities of an Ideal Model

An ideal model should explain molecular shapes, geometries, bond polarities, bond distances, various energy transitions and unique behaviour of molecules during chemical reactions.

MODERN THEORIES OF COVALENT BONDING

Various theories have been proposed to explain the nature of covalent bonding.

A few important of these theories are

A. Valence shell electron pair repulsion theory (VSEPR)
B. Valence bond theory (VBT)
C. Molecular orbital theory (MOT)

VALENCE SHELL ELECTRON PAIR REPULSION THEORY

- *This theory was proposed by Sidwick and Powell in 1940, to explain the shape of covalent molecules on the bases of electron pairs in the outer orbit of the central atom.*
- *Recently, Nylholm and Gillespie developed VSEPR theory to explain the shapes of molecules for non-transition elements.*

Basic Assumption

The electron pairs (both lone pairs and bond pairs) are arranged around the central atom to remain at a maximum distance apart to keep repulsions at a minimum.

Postulates of VSEPR theory

1. Both lone pair and bond pairs are involved in determining the geometry of molecules.
2. The electron pairs are arranged at a maximum distance around the central polyvalent atom to avoid repulsions.
3. A lone pair occupies more space than a bond pair.
4. The repulsion b/w electron pairs decreases in the following order

   Lone pair–lone pair > Lone pair–bond pair > bond pair–bond pair

   It is because a bond pair is attracted by both nuclei while a lone pair is attracted by only one nucleus, therefore, lone pair is less attracted by nucleus. Hence its spread out more in space than bond pairs and occupy more space. Thus, it exerts greater repulsions and compresses the bond pairs.
5. Double bonds and triple bonds occupy more space than a single bond.

   It is because, double and triple bonds contain higher electronic charge density, therefore, they occupy more space than one electron pair of single bond.
6. Multiple bonds (i.e. double or triple bond) behave as single bond in determining the geometry of molecule.

   It is because they also occupy the same region between the nuclei like a single bond.

APPLICATIONS OF VALENCE SHELL ELECTRON PAIR REPULSION THEORY

- VSEPR theory can predict the shapes of covalent molecules.
- Consider a central atom 'A'. It combines with two or more 'B' type atoms to give AB_2, AB_3, AB_4, AB_5, AB_6 type molecules.
- The number of 'B' atoms attached to 'A' depends upon the valency of 'A'.
- Thus, molecules can be divided into different categories as given in the following table

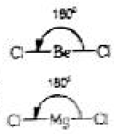
Table: Shapes of molecules according to VSEPR theory

Total No. of Electron pairs around central atom	No. of bond pairs	No. of lone pairs	Type	Arrangement of Electron pairs	Molecular geometry	Examples
2	2	0	AB_2	*Linear*	**Linear**	BeX_2, CdX_2, $MgCl_2$, $HgCl_2$
3	3	0	AB_3	*Triangular Planar*	**Triangular Planar**	BX_3
	2	1			**Bent or Angular**	$SnCl_2$, SO_2
4	4	0	AB_4	*Tetrahedral*	**Tetrahedral**	CH_4, CF_4, SiH_4, CCl_4
	3	1			**Triangular Pyramidal**	NH_3, PCl_3, PH_3, $AsCl_3$
	2	2			**Bent or Angular**	H_2O, H_2S
5	5	0	AB_5	*Triangular bipyramidal*	**Triangular bipyramidal**	PCl_5
6	6	0	AB_6	*Octahedral*	**Octahedral**	SF_6

1. Molecules With Two Electron Pairs (AB_2 Type)

Example: $BeCl_2$

- There are two electron pairs around the central Be atom.
- Both electron pairs are bond pairs.
- There is no lone pair.
- According to VSEPR theory the two electron pairs are present at 180° angle in order to have minimum repulsion between them. Thus arrangement of electron pairs is linear.
- The molecular geometry is determined by bond pairs only. So, $BeCl_2$ molecule is linear.



Other Examples

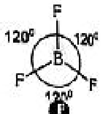
$MgCl_2$, $CaCl_2$, $SrCl_2$, $CdCl_2$, $HgCl_2$, CO_2 etc.

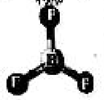
2. Molecules with three electron pairs

i) AB_3 TYPE: WITH NO LONE PAIR:

EXAMPLE BF_3

- There are three electron pairs around the central B atom.
- All three electron pairs are bond pairs.
- There is no lone pair.
- According to VSEPR theory, the three electron pairs are present at 120^0 angle in order to have minimum repulsion between them. Thus arrangement of electron pairs is triangular planar.
- The molecular geometry is determined by bond pairs only. So, BF_3 molecule is also triangular planar.





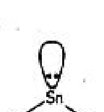
Other Examples

Hydrides of group III-A (AlH_3 , GaH_3 , InH_3) and their halides(BF_3 , $AlCl_3$) etc.

ii) AB_2 TYPE: WITH TWO BOND PAIRS AND ONE LONE PAIR:

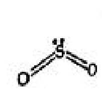
EXAMPLE: $SnCl_2$

- There are three electron pairs around the central Sn atom.
- Two electron pairs are bond pairs and one electron pair is lone pair.
- According to VSEPR theory, the three electron pairs are present in a triangular planar form in order to have minimum repulsion between them. Thus arrangement of electrons is triangular planar.
- The molecular geometry is determined by bond pairs only. So, $SnCl_2$ molecule is bent or angular. Since, lone pair exert greater repulsions on bond pairs, therefore, Cl – Sn – Cl bond angle is less than 120°.

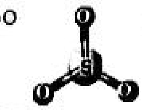


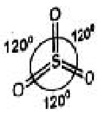
AB_2 WITH MULTIPLE BONDS

In SO_2, one corner of triangle is occupied by lone pair and other two are occupied by S=O bonds. Thus it has angular structure.



In SO_3, all corners of triangle are occupied by S=O bonds. Thus it has triagular structure (tiangular planar).



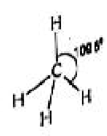


3. Molecules With Four Electron Pairs Around Central Atom

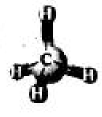
i) AB_4 TYPE: WITH NO LONE PAIRS

EXAMPLE: CH_4

- There are four electron pairs around the central C atom.
- All four electron pairs are bond pairs.



- There is no lone pair.
- According to VSEPR theory, the four electron pairs are present at 109.5^0 angle in order to have minimum repulsion between them. Thus arrangement of electron pairs is tetrahedral.
- The molecular geometry is determined by bond pairs only. So, CH_4 molecule is also tetrahedral.



In this hydogens are present at the corner of tetrahedron. Thus CH_4 molecule is tetrahedral. Each H – C – H bond angle is 109.5°.

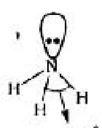
This structure is non – planar. It has four corners, four faces, six edges and six bond angles.

Other examples:

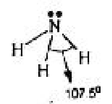
CCl_4 , SiH_4 , GeH_4 etc.

ii) AB_3L Type: WITH THREE BOND PAIRS AND ONE LONE PAIR

EXAMPLE: NH_3



- There are four electron pairs around the central N atom.
- Three electron pairs are bond pairs and one electron pair is lone pair.
- According to VSEPR theory, the three electron pairs are present in a tetrahedral form in order to have minimum repulsion between them. Thus arrangement of electrons is tetrahedral.
- The molecular geometry is determined by bond pairs only. So, NH_3 molecule is triangular pyramidal.
- The electronic configuration of N is



$$_7N\ 1s^2\ 2s^2\ 2p_x^1\ 2p_y^1\ 2p_z^1$$

- Since lone pair occupies more space than bond pairs. Therefore, lone pair present in 2s orbital of N exerts greater repulsions on bond pairs. Thus H – N – H bond angle reduces from 109.5° to 107.5°

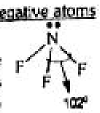
Other Examples

NF_3, PCl_3 , PH_3 , AsH_3 , SbH_3 , BiH_3 etc

Effect of Eelctronegativity on Bond Angle.

In compounds in which hydrogens of NH_3 are substituted by more electronegative atoms as NF_3 , bond angles are further reduced.

Reason: In NF_3, the polar N-F bond pulls the lone pair of N closer to the nucleus. Thus it exerts greater repulsions on bond pairs, hence bond angle is reduced to 102°. Further, bonding electrons are present closer to F, due to which mutual repulsions of bond pairs are also decreased.



(iii) AB_2L_2 TYPE: WITH TWO BOND PAIRS AND TWO LONE PAIRS.

EXAMPLE : H_2O

- There are four electron pairs around the central O atom.
- Two electron pairs are bond pairs and two electron pairs are lone pair.
- According to VSEPR theory, the two electron pairs are present in a triangular plane form in order to have minimum repulsion between them. Thus arrangement of electrons is tetrahedral.
- The molecular geometry is determined by bond pairs only. So, H_2O molecule is angular or bent.
- The electronic configuration of O is

$$_8O\ 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$$

- In water two lone pairs and two bond pairs are present. Thus it has three types of repulsions i.e. lone pair – lone pair, lone pair–bond pair and bond pair – bond pair.
- All the electron pairs form tetrahedron. Two of the corners of tetrahedron are occupied by lone pairs. Thus, H_2O molecule has angular or bent structure.
- In water, there are greater repulsions of lone pairs among themselves and with bond pairs. Thus H – O – H bond angle is reduced to 104.5°.

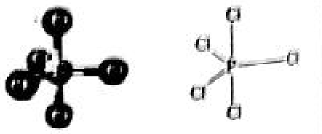
Other Examples

H_2Se, H_2S, H_2Se

4. Molecules with five electron pairs around Central Atom

The five electron pairs arrange in a triangular bipyramidal geometry

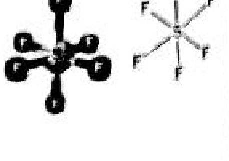
Example: PCl_5



5. Molecules with six electron pairs around Central Atom

The six electron pairs arrange in an octahedral geometry

Example: SF_6



Limitations of VSEPR theory

(i) It does not give reasons for the formation of bond.

(ii) It does not explain bond energies.

VALENCE BOND THEORY

It is based on the quantum–mechanical model of atom. It explains formation of bond, bond energies, bond length and shapes of molecules.

The basic assumption of V.B. theory is that

Half-filled valence atomic orbitals of combining atoms overlap to form covalent bonds.

The line between two nuclei is called bond axis or inter-nuclear axis.

Important Points

(i) The two overlapping orbitals must be valence orbitals and must be half filled.

(ii) Larger the overlap stronger the bond.

(iii) The direction of bond is determined by direction of overlapping orbitals.

(iv) Two electrons, present in bond orbital, must have opposite spins. Thus paired electrons stabilize themselves.

Valence bond theory describes two types of bond

Sigma Bond (σ-bond)

It is the single bond formed, when two partially filled atomic orbitals overlap in such a way that the probability of finding the electron is maximum around the line joining the two nuclei.

All single covalent bonds are σ-bond

Examples

1. Formation of H_2 molecule:

s – s Overlap

The electronic configuration of H is $1s^1$. 1s orbitals of two hydrogen atoms overlap with each other to form H – H bond. In this bond electron density is present between the nuclei. This bond is called σ-bond

2. Formation of HF molecule

s – p Overlap

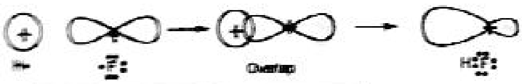
H – F bond is formed by pairing of electrons, one from H atom and one from F atom.

Electronic configurations of H and F are

$_1H \quad 1s^1$

$_9F \quad 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$

Thus, H and F need one electron each to complete their outermost shell. This is done by overlapping of 1s orbital of H with $2p_z$ orbital of F.



3. *Formation of F_2 molecule*

p – p Overlap

Electronic configuration of F is

$_9F \quad 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$

Thus, $2p_z$ orbitals of two F atoms overlap with each other to form F – F bond.

Pi – Bond (π bond)

The bond formed by side-to-side or parallel overlap of the p-orbitals. The bond in which greatest electron density is present above and below the internuclear axis.

For π-bond formation, the two overlapping orbitals must lie in the same plane.

Consider the π-bond formation by p-orbitals.

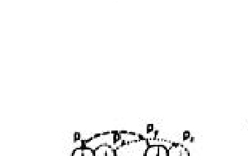
Examples: Formation of N_2 molecule

N_2 molecule is formed by combination of two nitrogen atoms.

The electronic configuration of N is

$_7N \quad 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

Two N atoms have half-filled $2p_x$, $2p_y$ & $2p_z$ orbitals. $2p_x$ orbitals of two N atoms overlap end-to-end to give a σ – bond, while two $2p_y$ orbitals and two $2p_z$ orbitals of two N atoms overlap to give two π-bond by parallel overlapping.



Thus there is one σ– bond and two π- bonds between two nitrogen atoms in N_2 molecule.

Sigma bond is formed by linear head-on-overlap, while pi bond is formed by parallel overlap. Therefore, in sigma bond there is larger overlap than pi bond. According to Valence Bond Theory, larger the overlap stronger the bond. Thus, sigma bond is stronger than pi bond.

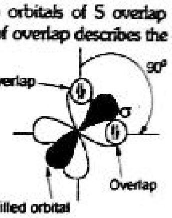
Geometry of H_2S Molecule

It is a non – linear molecule. In this H – S – H bond angle is about 92°

Electronic configuration of S is

$_{16}S \quad 1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^1 3p_z^1$

Two half-filled 3p orbitals of S overlap with two 1s orbitals of H atom to form H_2S molecule. Thus, idea of overlap describes the geometry of H_2S molecule.



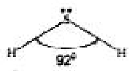


Figure: Bonding in H_2S showing overlap of orbitals

Atomic Orbital Hybridization and Shapes of Molecules

The process in which atomic orbitals of different energy and shape are mixed together to form a new set of equivalent orbitals of same energy and same shape is called hybridization.

The orbitals formed are called hybrid orbitals.

Importance

Concept of hybridization is used to explain equivalent tetravalency of C, bond angles in H_2O and NH_3 etc.

Energy for Excitation

In some cases, one electron is promoted from lower orbital to higher orbital to increase the number of unpaired electrons. The excited orbitals then undergo hybridization. The promotion of electron and hybridization is a simultaneous process. The energy required for excitation is compensated during hybridization and bond formation. Hybridization gives orbitals of new shape and orientation.

Types of Hybridization

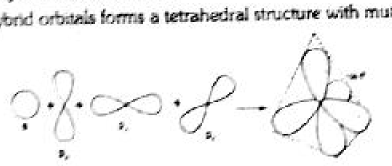
There are various types of hybridization depending upon the number and nature of orbitals taking part in hybridization. e.g., sp^3, sp^2, sp, dsp^2, dsp^3, d^2sp^3 etc.

s and p orbitals hybridize in the following ways.

sp^3 - Hybridization

In this, one s and three p atomic orbitals intermix to form four equivalent orbitals called sp3 hybrid atomic orbitals.

Four sp^3-hybrid orbitals forms a tetrahedral structure with mutual bond angles of 109.5^0.

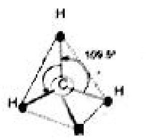


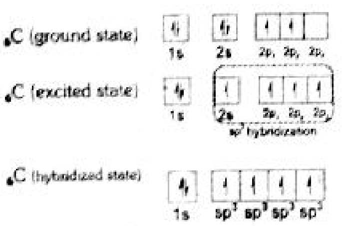
Four sp^3 hybrid orbitals

Figure: sp^3 hybridization

Example 1: CH_4 (Methane)

In CH_4, C undergoes sp^3 hybridization. This hybridization can be represented as





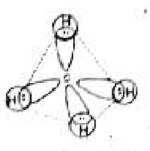
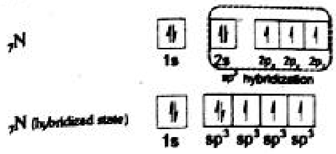


Figure: Four sp^3-s overlaps in tetrahedral structure of CH_4

- Each sp^3 – hybrid orbital has two lobes, one smaller and one larger. For simplicity smaller lobe is not usually shown.
- Four sp^3-hybrid orbitals of C are present at the corners of regular tetrahedron.
- Four sp^3-hybrid orbitals of C overlap with half-filled 1s orbitals of four H atoms to form CH_4 molecule with tetrahedral geometry. All the bond angles are of 109.5^0. The tetrahedral structure of CH_4 has four faces, four corners, six edges and six bond angles.

Example 2: NH_3

In NH_3, N undergoes sp^3 hybridization. One s and three p-orbitals of N hybridize to give four sp^3 hybrid orbitals. It can be represented as



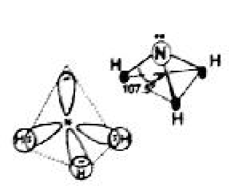
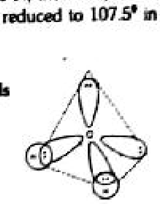


Fig: Four sp^3-s overlaps in pyramidal structure of NH_3

- Four sp^3 hybrid orbitals are present at the corners of regular tetrahedron.
- Three half-filled sp^3-hybrid orbitals of N overlap with half-filled 1s orbitals of three H atoms to form NH_3 molecule. While a lone pair is present at one corner of a tetrahedron. Thus NH_3 have pyramidal geometry in which hydrogen atoms form the base while lone pair form the apex.
- Since lone pair occupies more space than bond pairs and closer to N, therefore, exerts greater repulsions on bond pairs. Thus H – N – H bond angle is reduced to 107.5° in NH_3 from normal tetrahedral angle of 109.5°.

Example 3: H_2O

In H_2O, O undergoes sp^3 hybridization. One s and three p-orbitals of O hybridize to give four sp^3 hybrid orbitals. It can be represented as



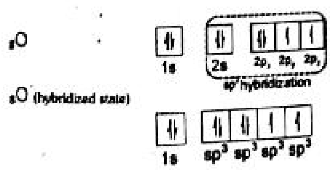


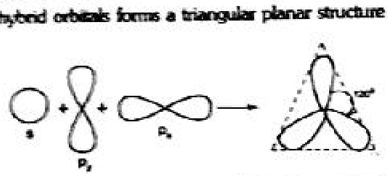
Figure: Four sp^3-s overlaps in angular structure of H_2O

- Four sp^3 hybrid orbitals are present at the corners of regular tetrahedron.
- Two half-filled sp^3-hybrid orbitals of O overlap with half-filled 1s orbitals of two H atoms to form H_2O molecule while two lone pairs are present at the corners of a tetrahedron. Thus H_2O has angular geometry.
- Since lone pair occupies more space than bond pairs and closer to O, therefore, exerts greater repulsions on bond pairs. Thus H – O – H bond angle is reduced to 104.5° in H_2O from normal tetrahedral angle of 109.5°.

sp^2 – Hybridization

In this, one s and two p atomic orbitals intermix to form three equivalent orbitals called sp^2 hybrid atomic orbitals.

Three sp^2-hybrid orbitals forms a triangular planar structure with mutual bond angles of 120°.



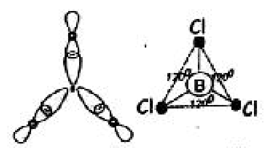
Example 1: BF_3

In BF_3, B undergoes sp^2 hybridization. This hybridization can be represented as

$_5B$ (ground state) [⇅] [⇅] [↑| |] — 1s, 2s, $2p_x$ $2p_y$ $2p_z$

$_5B$ (excited state) [⇅] [↑] [↑|↑|] — 1s, 2s, $2p_x$ $2p_y$ $2p_z$ — sp^2 hybridization

$_5B$ (hybridized state) [⇅] [↑|↑|↑] — 1s, sp^2 sp^2 sp^2



Fig(6.15) sp^2-s overlaps in triangular planar structure of BF_3

Fluorine has one half filled p-orbital. Three sp^2-hybrid orbitals of B overlap with half-filled $2p_z$ orbitals of three F atoms to form BF_3 molecule with triangular planar structure.

Example 2: C_2H_4

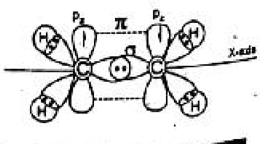
In C_2H_4 each C atom shows sp^2 hybridization.

This hybridization can be represented as

$_6C$ (ground state) [⇅] [⇅] [↑|↑|] — 1s, 2s, $2p_x$ $2p_y$ $2p_z$

$_6C$ (excited state) [⇅] [↑] [↑|↑|↑] — 1s, 2s, $2p_x$ $2p_y$ $2p_z$ — sp^2 hybridization

$_6C$ (hybridized state) [⇅] [↑|↑|↑] [↑] — 1s, sp^2 sp^2 sp^2, $2p_z$

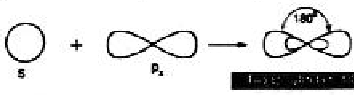


- Each C atom undergoes sp^2-sp^2 overlap with each other to form a σ- bond.
- Similarly each C also sp^2 – s overlap with H atoms to form C_2H_4 molecule with triangular planar structure.
- One unhybridized p-orbital of two carbon atoms overlap sideways to form a π–bond. In this bond probability of finding electron is maximum between the nuclei.

sp – Hybridization

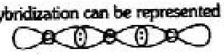
In this, one s and one p atomic orbitals intermix to form two equivalent orbitals called sp hybrid atomic orbitals.

The two hybrid orbitals are present at an angle of 180°.



Example 1: $BeCl_2$

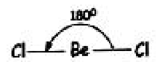
In $BeCl_2$, Be undergoes sp hybridization. This hybridization can be represented as



$_4Be$ (ground state) [⇅] [⇅] [| |] — 1s, 2s, $2p_x$ $2p_y$ $2p_z$

$_4Be$ (excited state) [⇅] [↑] [↑| |] — 1s, 2s, $2p_x$ $2p_y$ $2p_z$ — sp hybridization

$_4Be$ (hybridized state) [⇅] [↑|↑] — 1s, sp sp



Two sp-hybrid orbitals of Be are present at an angle of 180°. These orbitals overlap with half-filled $3p_z$ orbitals of two Cl atoms to form linear $BeCl_2$ molecule.

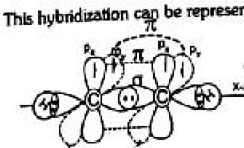
Example 2: C_2H_2

In C_2H_2 each C atom shows sp hybridization. This hybridization can be represented as

$_6C$ (ground state) [⇅] [⇅] [↑|↑|] — 1s, 2s, $2p_x$ $2p_y$ $2p_z$

$_6C$ (excited state) [⇅] [↑] [↑|↑|↑] — 1s, 2s, $2p_x$ $2p_y$ $2p_z$ — sp hybridization

$_6C$ (hybridized state) [⇅] [↑|↑] [↑|↑] — 1s, sp sp, $2p_y$ $2p_z$



- Each C atom undergoes sp–sp overlap with each other to form a σ–bond. Similarly, each C also sp–s overlaps with H atoms to form C_2H_2 molecule to form C_2H_2 molecule with linear structure.
- Two unhybridized p orbitals of two carbon atoms overlap sideways to form two π – bonds. Four electronic clouds of two π – bonds intermix and surround the sigma bond in the shape of a drum.

MOLECULAR ORBITAL THEORY

It is based on quantum mechanical model of atom. It considers molecule as a single unit. It's main points are

1. Atomic orbitals (AOs) combine to give new set of molecular orbitals (MOs), which are characteristic of the whole molecule
2. The molecular orbitals surround two or more nuclei of bonded atoms
3. Two atomic orbitals of combining atoms overlap with each other to give two molecular orbitals. One with lower energy is called bonding molecular orbital and the other with higher energy is called antibonding molecular orbital.
4. In bonding MOs, electron density is present between two nuclei while in antibonding MOs it is away from nuclei.
5. The number of MOs produced is always equal to the number of AOs combined.
6. The filling of molecular orbitals takes place according to Aufbau principal, Pauli's exclusion principle and Hund's rule.

Explanation

s – s Overlap

Consider two hydrogen atoms H_A and H_B. Each hydrogen atom has one electron in its 1s orbital. Two 1s orbitals of combining hydrogen atoms overlap with each other to give two molecular orbitals of different energy.

Low energy molecular orbital is called bonding sigma MO denoted by σ 1s and high energy molecular orbital is called antibonding sigma MO denoted by σ^*1s.

The bonding molecular orbital is symmetrical about the axis (molecular axis) joining the nuclei of bonded atoms.

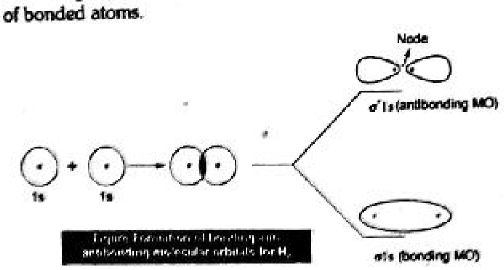


Figure: Formation of bonding and antibonding molecular orbitals for H_2

p – p overlap

Consider the overlap of p orbitals. Three p – orbitals are perpendicular to each other. Following overlap occurs between p – orbitals.

σ – Bond (Head On Approach):

The MO, which is symmetrical about the bond axis is called σ – MO

Or

The MO produced by the head on overlap of atomic orbitals are called σ – MO

When atomic orbitals combine head on σ – bonding MO and σ* – antibonding MO are produced.

Head on overlap of two $2p_x$ orbitals produces σ and σ* MOs.

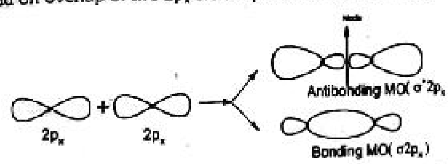


Figure: Head on overlap of two p orbitals

π – MO (Sideways Approach):

The MO, which is formed by sideways overlap of atomic orbitals and contains only one nodal plane on the nuclear axis is called π – MO

Bonding molecular molecular orbital $\pi(2p_y)$ and $\pi(2p_z)$ have zero electron density on the nuclear axis. It is called nodal plane. Electron density is uniformly distributed above and below the nodal plane.

Antibonding molecular orbitals $\pi^*(2p_y)$ and $\pi^*(2p_z)$ have least electron density in the π inter-nuclear region.

Since $2p_y$ and $2p_z$ are degenerate, therefore, $\pi(2p_y)$ and $\pi(2p_z)$ are also degenerate. Similarly $\pi^*(2p_y)$ and $\pi^*(2p_z)$ are also degenerate.

Thus six molecular orbitals are produced by overlap of two sets of p–orbitals. Three bonding and three antibonding.

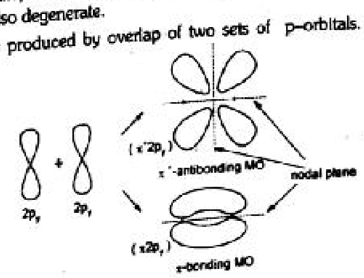


Figure: Sideways overlap of two p orbitals

The bond formed by linear (head on) overlap is called σ –bond. While the bond formed by sideways overlap is called π– bond.

Since three bonding orbitals are produced, therefore, p – orbitals can form three bonds: one sigma and two π– bonds.

Relative energies of MOs

- The energies of molecular orbitals are determined by spectroscopy.
- The energy of MOs of diatomic molecules such as O_2, F_2 and their positive and negative ions is in the following order

$$\sigma(1s)<\sigma^*(1s)<\sigma(2s)<\sigma^*(2s)<\sigma(2p_x)<\pi(2p_y)=\pi(2p_z)<\pi^*(2p_y)=\pi^*(2p_z)<\sigma^*2p_x$$

π 2p$_y$ and π2p$_z$ are of same energy. These are called degenerated orbitals.

- The energy of M.Os. of diatomic molecules such as N_2 , Be_2 ,C_2 etc. is in the following order.

$$\sigma(1s)<\sigma^*(1s)<\sigma(2s)<\sigma^*(2s)<\pi(2p_y)=\pi(2p_z)<\sigma(2p_x)<\pi^*(2p_y)=\pi^*(2p_z)<\sigma^*2p_x$$

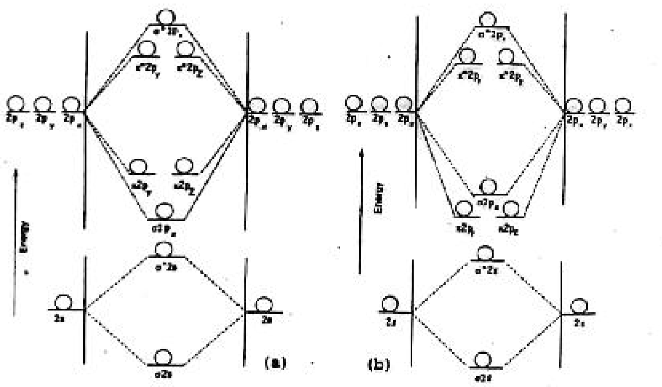


Fig. [illegible] Molecular orbital diagrams [illegible] (b) For [illegible] Be$_2$, B$_2$ and N$_2$

In N_2, B_2 and C_2, σ 2p$_x$ is higher in energy than π 2p$_y$ = π 2p$_z$. Why?

In case of N_2 , B_2 and C_2 , σ 2p$_x$ is higher in energy than π 2p$_y$= π 2p$_z$. It is due to mixing of 2s and 2p atomic orbitals.

The energy difference between 2s and 2p orbitals is small. Therefore, these are mixed together (hybridization of AO). Thus σ 2s and σ^* 2s do not have pure s – character.

Similarly, σ 2p$_x$ and σ^* 2p$_x$ MOs do not have pure p–character. All these four MOs gain sp-character. As a result, energy of these orbitals changes. σ 2s and σ^* 2s becomes more stable and are lowered in energy while σ 2p$_x$ and σ^* 2p$_x$ becomes less stable and are raised in energy.

Since π 2p$_y$= π 2p$_z$ are not involved in mixing, therefore, their energy remains same. Thus energy of σ 2p$_x$ is raised so much that it goes higher than π 2p$_y$= π 2p$_z$ bonding orbitals.

This mixing does not occur with O_2 , F_2 due to large energy difference between 2s and 2p$_x$ orbitals.

Energy differences between 2s and 2p orbitals are given below. These have been determined by spectroscopy.

Boron = 554 kJ/mol Carbon = 846 kJ/mol Nitrogen = 1195 kJ/mol

Oxygen = 1595 kJ/mol Fluorine = 2078 kJ/mol

BOND ORDER

The number of bonds formed between two atoms by overlap of atomic orbitals is called the bond order.

In MOT, the bond order is defined as

The half of the difference between the number of bonding electrons and anti-bonding electrons.

It is given by the formula

$$\text{Bond Order} = \frac{\text{No. of electron in bonding MO} - \text{No. of election in antibonding MO}}{2}$$

Generally, valence orbitals are considered in bond order calculations.

EXAMPLES

FIRST PERIOD ELEMENTS

Formation of H_2 molecule

- Electronic configuration of H is 1s[1].
- MO diagram of H_2 is shown in the fig.

H_2 molecule has two electrons both in (σ1s) orbital and forms a single covalent bond as shown in fig.

- Electronic configuration of H_2 is $\sigma(1s)^2$

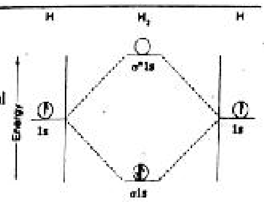


Figure: Molecular orbitals [illegible] H$_2$

- Bond order = $\frac{2-0}{2} = 1$

Thus, there is a single covalent between two hydrogen atoms in H_2 molecule.

Non-existence of He_2 molecule

- Electronic configuration of He is
  $_2He \quad 1s^2$
- Its MO diagram is shown in the fig.
- He_2 configuration is
  $\sigma(1s)^2 < \sigma^*(1s)^2$
- Bond Order $= \dfrac{2-2}{2} = 0$

Thus there is no bond i.e; no attractive force between two He atoms.
Hence Helium molecule (He_2) does not exist.

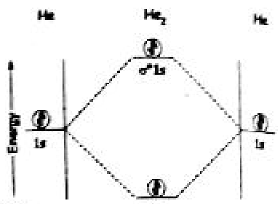


Fig: Molecular orbitals picture of He_2 (hypothetical)

SECOND PERIOD ELEMENTS

Formation of N_2 Molecule

- Electronic configuration of N is
  $_7N \ 1s^2 \, 2s^2 \, 2p_x^1 \, 2p_y^1 \, 2p_z^1$
- Electronic configuration of N_2 is

$\sigma(1s)^2 < \sigma^*(1s)^2 < \sigma(2s)^2 < \sigma^*(2s)^2 < \pi(2p_y)^2 = \pi(2p_z)^2 < \sigma(2p_x)^2$

- Since all the six electrons enter into three outermost bonding orbitals while no electrons enter into anitbonding orbitals. Thus

Bond Order$= \dfrac{6-0}{2} = 3$

Thus there is present triple bond between two nitrogen atoms in N_2 molecule. i.e. $N \equiv N$. One bond is σ- bond while two others are π- bonds.

Bond Energy of $N_2 = 941$ kJ / mol

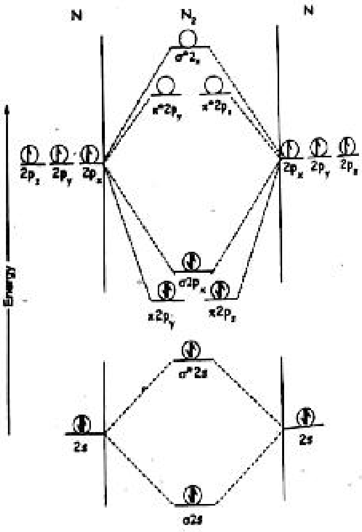


Figure: Molecular orbitals picture of N_2

Formation of O_2 Molecule

- Electronic configuration of O is

$_8O \ 1s^2 \, 2s^2 \, 2p_x^2 \, 2p_y^1 \, 2p_z^1$

- Electronic configuration of O_2 molecule is

$\sigma(1s)^2 < \sigma^*(1s)^2 < \sigma(2s)^2 < \sigma^*(2s)^2 < \sigma(2p_x)^2 < \pi(2p_y)^2 = \pi(2p_z)^2 < \pi^*(2p_y)^1 = \pi^*(2p_z)^1$

- Bond Order $= \dfrac{6-2}{2} = 2$

Thus, O_2 molecule has a double and between two oxygen atoms i.e; O=O

- O_2 has two unpaired electrons in π^*2p_y and π^*2p_z orbitals. Due to these unpaired electrons O_2 shows paramagnetic behaviour.
- The paramagnetic behaviour of O_2 cannot be explained by Valence Bond Theory. It is the main success of MOT.

Liquid O_2 is attracted towards the magnet.

Bond energy of $O_2 =$ 494 KJ / mol

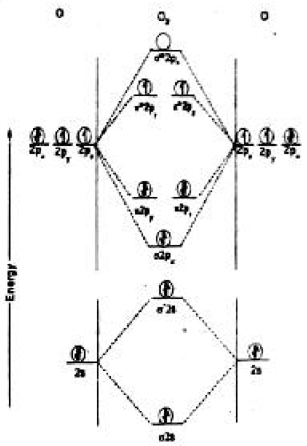


Figure: Molecular orbitals picture of O_2

In O_2^{2-}, two electrons are added, thus its paramagnetism finishes. Similarly in O_2^{2+}, two unpaired electrons are removed, thus its paramagnetism also finishes. Bond order of O_2^{2-} is one and O_2^{2+} is three.

BOND ENERGY, BOND LENGTH AND DIPOLE MOMENT

Bond Energy (Bond Enthalpy)

The average energy required to break one mole of similar bonds in a substance is called bond energy.

Units

It is expressed in kJ/mol

- It is the energy required to break an Avogadro's number of bonds. Same amount of energy is released when an Avogadro's number of bonds is formed.
- Experimentally bond energies are determined by calorimetry or spectroscopy.
- ***The enthalpy change in splitting a molecule into its component atoms is called enthalpy of atomization***

Ionic Character and Bond Energy

Bond energy is a measure of strength of bond. Strength of bonds depend upon

- Electronegativity difference of bonded atoms
- Sizes of atoms
- Bond length

Table 6.3 Average bond enthalpies of some important bonds

Bond	Bond energy (kJmol⁻¹)	Bond	Bond energy (kJmol⁻¹)	Bond	Bond energy (kJmol⁻¹)	Bond	Bond energy (kJmol⁻¹)
C–C	348	H–H	436	O–O	146	Si–H	323
C=C	614	H–F	567	O=O	495	Si–Si	226
C≡C	839	H–Cl	431	O–H	463	Si–C	301
C–H	413	H–Br	366	O–F	190	Si–O	368
C–N	293	H–I	299	O–Cl	203	F–H	155
C=N	615	N–N	163	O–I	234	Cl–F	253
C≡N	891	N=N	418	S–S	266	Cl–Cl	242
C–O	358	N≡N	941	S=S	418	Br–F	237
C=O	799	N–H	391	S=O	523	Br–Cl	218
C≡O	1072	N–O	201	S–H	339	Br–Br	193
C–F	485	N–F	272	S–F	327	I–Cl	208

A polar covalent bond is stronger than a non-polar covalent bond.

Consider the greater strength of HCl, due to its polar(ionic) character.

- The H – H bond energy is 436 kJ/mol

i.e. $H + H \rightarrow H_2 \quad \Delta H = -436$ kJ/mol

Thus 6.02×10^{23} bonds have energy $= 436$ kJ

1 bond will have energy $= \dfrac{436}{6.02 \times 10^{23}} = 72.42 \times 10^{-23}$ kJ

Since each hydrogen atom contribute equally, therefore, contribution of each hydrogen will be 36.21×10^{-23} kJ.

- Similarly Cl – Cl bond energy is 240 kJ/mol and for one bond it is 39.86×10^{-23} kJ. Thus each Cl atom will contribute 19.93×10^{-23} kJ.

- Hence In case of H – Cl, bond energy must be $36.28 \times 10^{-23} + 19.93 \times 10^{-23} = 56.31 \times 10^{-23}$ kJ/molecule

- For one mole it will be 338.9 kJ/mol. But actually it is 432 kJ/mol. This increase in bond energy is due to polar character of H – Cl bond.

Note:

- ***Bond energies generally decrease with decrease in electronegativity difference of the bonded atoms.***

Example: In H – F, H – Cl, H – Br and H – I, greatest E.N. difference is in H – F bond i.e. 2.1, while in H – I, the E.N. difference is the least i.e.0.4.

Hence, H – F has greatest bond energy (568 KJ/mol) while that of HI is the least (299 kJ/mol)

- ***Relative electronegativities can be determined*** by noting difference between experimental and calculated bond energies. e.g. in case of HX, this difference is largest for HF and least for HI. It shows that HF is more ionic than HI.

Table 6.4 Comparison of experimental and theoretical bond energies

Bond	Bond energies (kJ mol⁻¹) X = F	X = Cl	X = Br	X = I
X – X	155	242	193	151
H – X (calculated)	293	236	311	291
H – X (observed)	567	431	366	299
Difference	274	95	55	8

- ***The order of ionic character is***

HF > HCl > HBr > HI

- Bond energies can be used to determine heats of gaseous reactions of covalent compounds.
  - ***Polar covalent bonds have high bond energy than non-polar covalent bonds.***
  - ***Shorter bonds have higher bond energies.***

    e.g. The bond energies of C≡C, C=C and C – C are in the order

    $$C \equiv C > C = C > C - C.$$

    Thus triple bond is stronger than double bond which is stronger than single bond. However, bond energy of triple bond is not thrice of single bond. Similarly bond energy of double bond is not double than single bond. Thus it shows that sigma bond is stronger than pi bond.
  - ***Bond energy decreases down the group, due to increase in bond length*** *for a* ***particular type of bond.***

BOND LENGTH

The average distance between the nuclei of two atoms forming a covalent bond is called bond length

Units

In SI system bond lengths are expressed in pm (1pm = 10^{-12} m).

The bond lengths are measured by physical methods. e.g. electron diffraction, X-ray diffraction or spectral studies.

Due to vibratory motion of atoms, bond lengths are not constant,. Thus measured bond length is actually the average value.

The covalent bond length of a particular bond is almost independent of the nature of molecules. e.g. in most aliphatic hydrocabons C – C bond length is 154 pm. Same bond length is present in diamond as well.

Relationship of Covalent Radii with Bond Length

One half of the distance between nuclei of two similar bonded atoms is called Covalent Radius.

Covalent radii of different elements are additive in nature.

Example:

Covalent radius of Cl is 99 pm, which is half of Cl – Cl bond length i.e.198 pm.

Similarly

Covalent radius of C is 77 pm, which is half of C – C bond length i.e.154 pm.

Thus C – Cl bond length must be 99 + 77 = 176 pm.

However, in certain cases, this rule does not apply.

Example: By adding covalent radii of Si (117 pm) and F (64 pm), the expected bond length of Si – F in SiF_4 is 181 pm but actual value is 154 – 159 pm.

This deviation is due to difference in electronegativity of the bonded atoms.

<u>Generally, greater the electronegativity difference, shorter the bond</u>

Thus calculated values are always higher than actual values due to electronegativity difference. It is because, ionic character is produced in the bond. The poles attract each other and bond length becomes shorter.

Table 6.5 Some selected bond lengths along with hybridization of central atom

Compound	Hybridization	Bond	Bond length (pm)
BF_3 (Boron trifluoride)	sp^2	B – F	130
BCl_3 (Boron trichloride)	sp^2	B – Cl	175
SiH_4 (Monosilane)	sp^3	Si – H	148
SiF_4 (Silicon tetrafluoride)	sp^3	Si – F	155
C_2H_6 (Ethane)	sp^3	C – C	154
C_2H_4 (Ethene)	sp^2	C = C	133
C_2H_2 (Ethyne)	sp	C ≡ C	120
$(CH_3)_2C=O$ (Acetone)	sp^2	C = O	122

Relationship of Hybridization with Bond Length

In general <u>bonds are shortened by increasing s – character</u> of the hybrid orbitals. It is because s-orbital has smallest mean radius.

e.g. Bond	Hybridization	% s – Character	Length (pm)
C – C in ethyne	sp	50%	120
C – C in ethene	sp^2	33.33%	133
C – C in ethane	sp^3	25%	154

Relationship Of Multiple Bonding With Bond Length

π – bonding also reduces the inter-nuclear bond distance.

Generally, triple bond is shorter than a double bond, which, in turn is shorter than a single bond.

e.g.

Bond	Bond length (pm)
C – C	154
C = C	133
C ≡ C	120

Trends in Periodic Table

Along Period

Generally, bond length decreases from left to right in a periodic table due to decrease in atomic size and increase in nuclear charge.

e.g. bond length of C – C is greater than N – N bond length.

In a Group

Generally, bond length increases down the group due to increase in atomic size.

e.g. Si – Si bond length is more than C – C bond length.

P – P bond length is more than N – N bond length.

It is because due to increase in atomic radius, effective nuclear charge decreases on electrons. Thus bond length increases.

DIPOLE MOMENT

"The product of the magnitude of one of the charges (positive or negative) and the distance between their centers is called dipole moment".

Explanation

The bond between two atoms of different electronegativities is polar i.e. have positive and negative poles. This produces polarity in the molecule.

The separation of charges on bonded atoms is called a dipole. It is measured in terms of dipole moment defined as

Let if 'q' is the magnitude of one of the charges and 'r' is the distance between them, then

$$\mu = q \times r$$

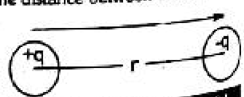


Figure: [illegible]

The dipole moment is a vector quantity. It is represented by an arrow, directed form electropositive end to the electronegative end of dipole.

For polyatomic molecules, the net dipole moment is the resultant of vector addition of individual bond moments.

[illegible]

- SI unit of dipole moment is mC (meter coloumb).
- Thus for a unit negative charge at a distance of 100 pm from a unit positive charge, we have

$$\mu = (1.6022 \times 10^{-19} C) \times (100 \times 10^{-12} m) = 1.6022 \times 10^{-29} mC \quad (1)$$

- mC is a bigger unit. Generally, smaller unit Debye (D) is used.

$$1D = 10^{-18} \text{ esu cm.}$$

$$\text{or} \quad 1D = 3.336 \times 10^{-30} mC \quad (2)$$

Thus from eq (1) and (2)

$$\mu = \frac{1.6022 \times 10^{-29}}{3.336 \times 10^{-30}} = 4.8D$$

APPLICATIONS

Dipole Moments and Molecular Structure

Dipole moment measurements help to determine the shape of molecules.

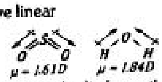
Diatomic molecules

Diatomic molecules are always linear.

e.g. CO has a linear structure and its dipole moment is 0.12 D.

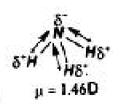
Triatomic Molecules

Both CO_2 and CS_2 has zero dipole moment. Thus these have linear structure, in which one dipole cancels the effect of other.



Dipole moment of SO_2 and H_2O are 1.64 D and 1.84 D respectively. It shows that SO_2 and H_2O have angular structure because one dipole does not cancel the effect of other.

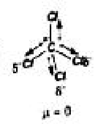
Tetratomic Molecules

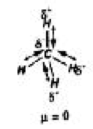


NH_3 has dipole moment, which shows that the individual bond mom ents do not cancel the effect of each other. It is because NH_3 has Pyramidal Structure.

Pentatomic Molecules

Both CCl_4 and CH_4 have no dipole moment which suggests a regular tetrahedral structure for them.





Percentage Ionic Character

Experimental dipole moments can be used to determine the %age ionic character of bond

The formula is

$$\%\text{age ionic character} = \frac{\mu_{obs}}{\mu_{ionic}} \times 100$$

Where μ_{obs} = Experimental dipole moment

μ_{ionic} = Dipole moment calculated on the basis of 100% charge separation

Table 6.6 Dipole moments of some substances in Debyes

Compound	Dipole moment (D)
H_2	0.00
HCl	1.03
HBr	0.78
HI	0.38
H_2O	1.85
H_2S	0.95
NH_3	1.49
SO_2	1.61
CO_2	0.00
CO	0.12
NO	0.16
H_2O_2	2.20
CH_4	0.00
CH_3F	1.81
CH_3Cl	1.45
CH_3Br	1.85
CH_3I	1.35
C_2H_5OH	1.69

Example 1:

The observed dipole moment of HF is 1.90D. The distance between the charges is 0.917×10^{-10}m. Find the percentage ionic character of the bond.

Solution

Unit positive charge = 1.6022×10^{-19} C

Charge = q = 1.6022×10^{-19} C

Bond length = r = 0.917×10^{-10} m

μ_{obs} = 1.90 D

μ_{ionic} = ?

% ionic character = ?

$$\mu_{ionic} = q \times r = 1.6022 \times 10^{-19}\,C \times 0.917 \times 10^{-10}\,m$$

$$= 1.469 \times 10^{-29}\,mC$$

Since $1\,D = 3.336 \times 10^{-30}$ mC

$$\text{Therefore } \mu_{ionic} = \frac{1.469 \times 10^{-29}}{3.336 \times 10^{-30}} = 4.4\,D$$

$$\text{Thus } \%\text{ ionic character} = \frac{1.90}{4.4} \times 100 = 43.2\,\%$$

Hence, 43% of HF bond is ionic in nature and 57% is covalent. The bond is mainly covalent.

EFFECTS OF BONDING ON THE PHYSICAL PROPERTIES OF COMPOUNDS

The properties of substances depend upon the types of bonding present in them.

SOLUBILITY

Ionic Compounds

- Ionic compounds are soluble in water but insoluble in non-aqueous solvents
- It is because polar water molecules detach cations and anions from the crystal lattice by electrostatic attractions. Thus, ionic compounds are dissolved by hydration of ions.
- The energy released during hydration is used to break the lattice.
- *Only those crystals are dissolved in water, for which, energy produced during hydration is greater than lattice energy, so that it can break the lattice.*
- Many ionic crystals do not dissolve in water because attraction of water molecules cannot overcome the attraction between ions.
- Ionic compounds are not dissolved in non-polar solvents like benzene and hexane.

Covalent Compounds

- Generally covalent compounds dissolve in non-polar organic solvents e.g. benzene, ether etc.
- In this case attraction of solvent molecules with the compounds break the intermolecular forces.
- Most covalent compounds are insoluble in H_2O. Few compounds are dissolved by hydrogen bonding.

Directional Nature and Isomerism

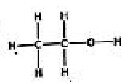
- **Ionic Compounds**

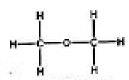
  Ionic compounds do not show isomerism because ionic bonds are non-rigid and non-directional.

- **Covalent compounds**

  Covalent compounds show isomerism because covalent bonds are rigid and directional

  e.g. C_2H_6O shows structural isomerism


ethanol


dimethyl ether

Compounds having same molecular formula but different structures and properties are called isomers and the phenomenon is called isomerism

- **Ionic Compounds**

  Reactions of ionic compounds are very fast

  It is because ionic compounds exist as ions in aq. solution. Chemical reactions between ions occur rapidly.

  e.g. By adding $AgNO_3$ solution to NaCl solution, white ppt of AgCl are produced at once.

  In this reaction, both $AgNO_3$ and NaCl are in ionized form. Therefore no bond is to be broken. Only few bonds are formed. Thus reaction occurs rapidly

- **Covalent Compounds**

  Reactions of covalent compounds are generally slow. Because no electrical forces are present in them to speed up the reaction and energy is required to break bonds and form new bonds. The molecules undergo a chemical change as a whole.

  Covalent compounds show many types of reactions which depends upon the way of reaction and kind of reaction.

OBJECTIVE AND SHORT ANSWER QUESTIONS (EXERCISE)

Q1. Select the correct statement.

(i) An ionic compound A^+B^- is most likely to be formed when (Lahore board, 2013)

(a) The ionization energy of A is high and electron affinity of B is low.

(b) The ionization energy of A is low and electron affinity of B is high.

(c) Both the ionization energy of A and electron affinity of B are high.

(d) Both the ionization energy of A and electron affinity of B are low.

(ii) The number of bonds in nitrogen molecules is

(a) one σ and one π (b) one σ and two π

(c) three sigma only (d) two σ and one π

(Rawalpindi Board, 2010, 2012) (D.G. Khan Board, 2011, 2012) 2011 A (Sargodha Board, 2012) (Lahore board, 2014) (Faisalabad Board, 2013)

(iii) Which of the following statements is not correct regarding bonding molecular orbitals.

(a) Bonding molecular orbitals possess less energy than atomic orbitals form which they are formed.

(b) Bonding molecular orbitals have low electron density between the two nuclei.

(c) Every electron in the bonding molecular orbitals contributes to the attraction between atoms.

(d) Bonding molecular orbitals are formed when the electron waves undergo constructive interference.

(iv) Which of the following molecules has zero dipole moment?

(a) NH_3 (b) $CHCl_3$ (c) H_2O (d) BF_3

(Multan Board, 2011) (D.G. Khan Board, 2012) (Gujranwala board, 2014)

(v) Which of the hydrogen halides has the highest percentage of ionic character

(a) HF (b) HBr (c) HCl (d) HI

(Faisalabad Board, 2007) (D.G. Khan Board, 2009, 2012) (Rawalpindi Board, 2009) (Faisalabad Board, 2009, 2013) (Multan Board, 2010, 2012) (Rawalpindi board, 2011) (Sargodha Board, 2012, 2013, 2014) (Gujranwala board, 2012, 2014)

(vi) Which of the following molecules has unpaired electrons in antibonding molecular orbitals

(a) O_2^{2+} (b) N_2^{-2} (c) B_2 (d) F_2

(Lahore Board, 2008) (Faisalabad Board, 2008) (Multan Board, 2008) (Bahawalpur Board, 2009, 2011) (Multan Board, 2010) (Rawalpindi board, 2012) (Sargodha Board, 2011) (D.G. Khan Board, 2012) (Gujranwala board, 2009, 2013)

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans. (b) Ionic bond is formed by complete transfer of electron from one atom to another. Hence, ionization energy of donor atom must be low to loose electron easily and electron affinity of acceptor atom must be high to accept electron.	**(ii) Ans (b)** In N_2 molecule, there are three bonds between two nitrogen atoms. one bond is sigma and other bond is pi-bond.
(iii) Ans: (b) According to MOT, when two atomic orbitals overlap with each other they form two molecular orbitals. Bonding MO and antibonding MO. In bonding MO, electron density is maximum between the nuclei while in antibonding MO, electron density is minimum between the nuclei. Therefore, [b] is correct	**(iv) Ans: (d)** NH_3, H_2O and $CHCl_3$ are all unsymmetrical molecules. Their individual bond moments do not cancel the effect of each other, therefore, all these have dipole moment. However, BF_3 has symmetrical structure. Its structure is triangular planar. In this structure individual bond moments cancel the effect of each other. Hence, BF_3 has zero dipole moment.
(v) Ans: (a) The polarity of a bond depends upon the difference of electronegativity between the two atoms. Since in HF, electronegativity difference is greatest, therefore, bond between H and F is highly polar. It has highest dipole moment of all. Thus, It has highest % ionic character.	**(vi) Ans: (b)** In B_2 and F_2 molecules, all the electrons are paired. In O_2 , two unpaired electrons are present in antibonding MO. However, when these two electrons are removed, O_2^{2+} is produced which has no unpaired electrons. In N_2 , no unpaired electrons are present. However, when two electrons are added to it, N_2^{2-} is produced which has two unpaired electrons in antibonding molecular orbitals just like O_2. For MO diagrams see Q12(b) part and Section 6.4.6

Q2. Fill in the blanks

(i) The tendency of atoms to attain maximum of eight electrons in the valence shell is called _____.

(ii) The geometrical shape of $SiCl_4$ and PCl_3 can be explained on the basis of _____ hybridization.

(iii) The VSEPR theory stands for _____.

(iv) For N_2 molecule, the energy of σ $2p_x$ orbital is _____ than π $2p_y$ orbital.

(v) The paramagnetic property of O_2 is well explained on the basis of MO theory in terms of the presence of _____ electrons in two MO orbitals.

(vi) The bond order of N_2 is _____ while that of Ne_2 is _____.

(vii) The value of dipole moment for CS_2 is _____ while for SO_2 is _____.

Answers:

(i) eight, octet rule	(ii) sp^3	(iii) valence shell electron pair repulsion
(iv) greater	(v) unpaired	(vi) three, zero
		(vii) zero, 1.61

Q3. Classify the statements as true of false. Explain the reason.

(i) The core of an atom is the atom minus its valence shell.

(ii) The molecules of nitrogen $N \equiv N$ and acetylene $HC \equiv HC$ are not isoelectronic.

(iii) There are four coordinate covalent bonds in NH_4^+ ion.

(iv) A σ – bond is stronger than a π – bond and electrons of σ – bond are more diffused than π – bond

(v) The bond energy of hetero diatomic molecules increases with the decrease in the electronegativities of the bonded atoms.

(vi) With increase in bond order, bond length decreases and bond strength increases.

(vii) The first ionization energies of the elements rise steadily with increasing atomic number from top to bottom is a group.

(viii) A double bond is stronger than single bond and a triple bond is weaker than a double bond.

(ix) The bonds formed between the elements having electronegativity difference more than 1.7 are always covalent in nature.

(x) The repulsive force between the two bonding pairs is less than that between the two lone pairs.

(xi) The number of covalent bonds an atom can form is related to the number of unpaired electrons it has.

(xii) The rules which govern the filling of electrons into the atomic orbitals also govern filling of electrons into the molecular orbitals.

Answers:

(i) True	(ii) False	(iii) False	(iv) False
(v) False	(vi) True	(vii) False	(viii) False
(ix) False	(x) True	(xi) True	(xii) True

Q4. What is a chemical bond? Discuss the formation of ionic and covalent bonds.

Page 324 (Ionic Bond) and Page 326 (Covalent Bond)

Q5. (a) Define ionization energy and electron affinity. How these quantities change with an increase in the mass number?

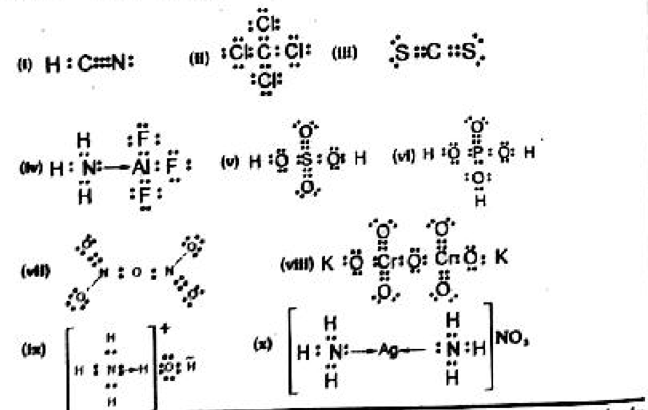
Page 319 (Ionization energy) and Page 321 (electron affinity)

(b) Explain, what do you understand by the term electronegativity? Discuss its variations in the periodic table. How does it affect the bond strength?

Page 323

Q6. Write the Lewis structures for the following compounds:

(i) HCN (ii) CCl_4 (iii) CS_2 (iv) $H_3N\ AlF_3$ (v) H_2SO_4 (vi) H_3PO_4
(vii) N_2O_5 (viii) $K_2Cr_2O_7$ (ix) NH_4OH (x) $Ag(NH_3)_2NO_3$



Q7. (a) Explain qualitatively the valence bond theory. How does it differ from molecular orbital theory?

Page 323 (For Valence Bond Theory)

	Valence Bond Theory		Molecular Orbital Theory
1.	In VBT only valence electrons are involved in bond formation	1.	In MOT, all electrons of combining atoms are involved in bond formation
2	In VBT, the two combining atoms do not loose their identity	2.	In MOT, the two atoms lose their identity
3	It does not explain the paramagnetic behaviour of molecules e.g., O_2 molecule	3.	In explains the paramagnetic behaviour
4	It does not give idea about the bond order	4.	It give idea about bond order. So we can determine whether the bond is single, double or triple or even in fraction
5	It does not explain the non-existence of He_2 molecule.	5.	It explains the non-existence of He_2 molecule.

(b) How the bonding in the following molecules can be explained with respect to valence bond theory?

Cl_2, O_2, N_2, HF, H_2S

Formation of Cl_2 molecule

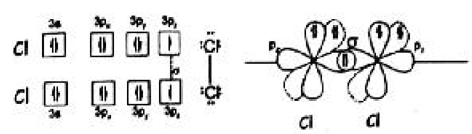
Cl_2 molecule is formed by two chlorine atoms.

The electronic configuration of Cl is

$_{17}Cl$ $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p_x^2\ 3p_y^2\ 3p_z^1$

Two Cl atoms have half-filled $3p_z$ orbitals. These orbitals overlap to give Cl_2 molecule with a single bond (σ - bond) between two Cl atoms.

Diagrammatically, formation of Cl_2 molecule can be represented as



Formation of HF molecule

HF molecule is formed by combination of hydrogen and fluorine atoms.

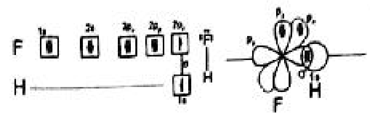
The electronic configurations of F & H are

$_9F$ $1s^2\ 2s^2\ 2p_x^2\ 2p_y^2\ 2p_z^1$

$_1H$ $1s^1$

According to V.B.T. half-filled $2p_z$ orbital of F atom overlaps with half-filled 1s orbital of H to form a σ -bond and thus HF molecule is formed.

Diagrammatically, formation of HF molecule can be represented as



Formation of O_2 molecule

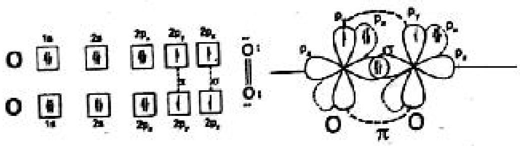
O_2 molecule is formed by combination of two oxygen atoms.

The electronic configuration of O is

$_8O$ $1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

Two O atoms have half-filled $2p_y$ & $2p_z$ orbitals. $2p_y$ orbitals of two O atoms overlap head on to give a σ – bond, while two $2p_z$ orbitals of two O atoms overlap to give a π – bond by parallel overlapping. Thus there is one σ– bond and one π– bond between two oxygen atoms in O_2 molecule.

Diagrammatically, formation of O_2 molecule can be represented as



Formation of N_2 molecule

N_2 molecule is formed by combination of two nitrogen atoms.

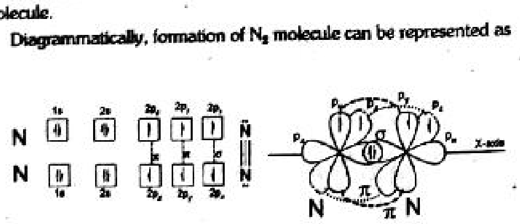
The electronic configuration of N is

$_7N\ 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$

Two N atoms have half-filled $2p_x$, $2p_y$ & $2p_z$ orbitals. $2p_x$ orbitals of two N atoms overlap head on to give a σ – bond, while two $2p_y$ orbitals and two $2p_z$ orbitals of two N atoms overlap to give two π – bond by parallel overlapping.

Thus, there is one σ– bond and two π– bonds between two nitrogen atoms in N_2 molecule.

Diagrammatically, formation of N_2 molecule can be represented as



Formation of H_2S

Page 339

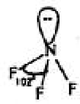
Q8. Explain VSEPR theory. Discuss the structures of CH_4, NH_3 and H_2O with reference to this theory and hybridization schemes?

Page 331 (VSEPR theory) and Page 340, 341 (hybridization of CH_4, NH_3 and H_2O)

Q9. The molecules of NF_3 and BF_3 all have molecular formula of the type XF_3. But they have different structural formulas. Keeping in view VSEPR theory sketch the shape of each molecule and explain the origin of difference in shapes.

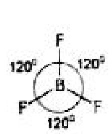
<u>NF_3</u>

In NF_3, nitrogen is sp^3-hybridized. There are four electron pairs present around nitrogen atom. It forms three covalent bonds with three fluorine atoms. There is one lone pair present on nitrogen atom. Hence, according to VSEPR theory, it will have a triangular pyramidal structure like NH_3. However, bond angle in NF_3 is 102°, which is less than that of NH_3 i.e., 107.5°. It is because F is more electronegative than N. Therefore, polarity of N –F bond pulls the lone pair of N closer to the nucleus. Thus, it exerts greater repulsions on bond pairs, hence bond angle is reduced to 102°.



<u>BF_3</u>

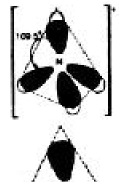
In BF_3, B is sp^2-hybridized. It is surrounded by three electron pairs. It forms three covalent bonds with three fluorine atoms. There is no lone pair on boron. Three electron pairs are present at a maximum angle of <u>120°</u> from each other in order to have minimum repulsion between them and form trigonal planar geometry. Thus BF_3 molecule is trigonal planar with bond angle of 120°.



Q10. The species NH_2^-, NH_3, NH_4^+ have bond angles of 105°, 107.5° and 109.5° respectively. Justify these values by drawing their structures.

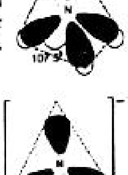
<u>NH_4^+</u>

In NH_4^+, nitrogen is sp^3-hybridized. It forms three covalent bonds and one co-ordinate covalent bond with hydrogen atoms. There is no lone pair present on nitrogen atom. Hence, according to VSEPR theory, it will have a regular tetrahedral structure with bond angle of 109.5°.



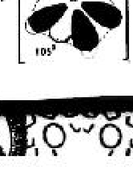
<u>NH_3</u>

In NH_3, nitrogen is sp^3-hybridized. It forms three covalent bonds with hydrogen atoms. There is also present a lone pair present on nitrogen atom. Hence, according to VSEPR theory, it will have a triangular pyramidal structure. Since lone pair exerts more repulsions on bond pairs. Hence, the bond angle will be reduced from 109.5° to 107.5°.



<u>NH_2^-</u>

In NH_2^-, nitrogen is sp^3-hybridized. It forms two covalent bonds with hydrogen atoms. There are also present two lone pairs on nitrogen atom.



Hence, according to VSEPR theory, it will have a bent structure. Since two lone pair exert more repulsions on bond pairs. Hence, the bond angle will be reduced from 109.5^0 to 105^0.

Q11. (a) Explain atomic orbital hybridization with reference to sp^3, sp^2 and sp modes of hybridizations for PH_3, C_2H_4 and C_2H_2. Discuss geometries of CCl_4, PCl_3 and H_2S by hybridization of central atoms.

Page 339

(b) The linear geometry of $BeCl_2$ suggests that central Be atom is sp-hybridized. What type of hybridization a central atom undergoes, when the atoms bonded to it are located at the corners of (i) an equilateral triangle, (ii) a regular tetrahedron and (iii) triangular bipyramid?

An equilateral triangle – sp^2 hybridization
A regular tetrahedron – sp^3 hybridization
A triangular bipyramid – dsp^3 hybridization

Q12. (a) Give the basis of the molecular orbitals theory and discuss the molecular orbitals configurations of the following molecules.

(i) He_2	Page 348
(ii) O_2	Page 349

(b) How does molecular orbital theory explain the paramagnetic character of O_2, O_2^{2+} and O_2^{2-} molecules?

Formation Of O_2 Molecule.

Electronic configuration of O is

$_8O\ 1s^2\ 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$

Thus, there are sixteen electrons in O_2 molecule.

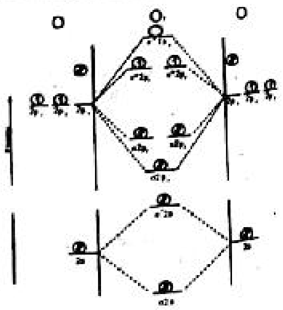
O_2 has two unpaired electrons in π^*2p_y and π^*2p_z orbitals. Due to these unpaired electrons O_2 shows paramagnetic behaviour.

Electronic configuration of O_2 molecule is

$\sigma(1s)^2 < \sigma^*(1s)^2 < \sigma(2s)^2 < \sigma^*(2s)^2 <$
$\sigma(2p_x)^2 < \pi_y(2p_y)^2 = \pi_z(2p_z)^2 < \pi^*_y(2p_y)^1 = \pi^*_z(2p_z)^1$

Liquid O_2 is attracted towards the magnet.

$$\text{Bond Order} = \frac{6-2}{2} = 2$$



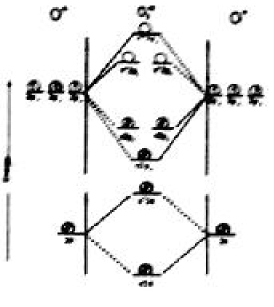
Formation of O_2^{+2} Ion.

In O_2^{+2} ion, two electrons are removed.

Thus, there are fourteen electrons in O_2^{+2} ion.

O_2^{+2} has no unpaired electrons in any orbital. Due to this unpaired electrons O_2^{+2} shows diamagnetic behaviour. i.e., it is not attracted towards magnet.

$$\text{Bond Order} = \frac{6-0}{2} = 3$$



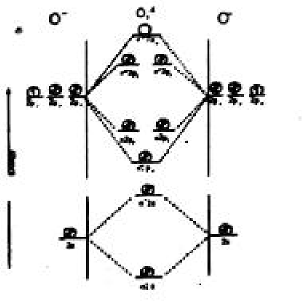
Formation of O_2^{-2} Ion.

In O_2^{-2} ion, two electrons are added.

Thus, there are Sixteen electrons in O_2^{-2} ion.

O_2^{-2} ion no unpaired electrons in any orbital. Due to this O_2^{-2} shows diamagnetic behaviour. I.e., it is not attracted towards magnet.

$$\text{Bond Order} = \frac{6-4}{2} = 1$$



Q13. (a) Sketch the molecular orbital pictures of

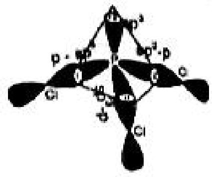
(a) $\pi(2p_x)$ and $\pi^*(2p_x)$	*Page 345*
(b) O_2, O_2^{2+}, O_2^{2-}	*Q 12*
(c) He_2 and Ne_2	

Page 348, MO diagram of Ne_2 is just like O_2. Only elelctronic configuration is different.

(b) Sketch the hybrid orbitals of the species, PCl_3, SF_6, $SiCl_4$ and NH_4^+.

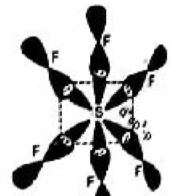
PCl_3

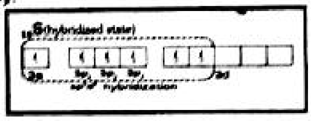
In PCl_3, P is sp^3-hybridized. P has four sp^3-hybrid orbitals. Its three hybrid orbitals overlap with p-orbitals of three chlorine atoms to form three covalent bonds. One hybrid orbital of P contains lone pair. Thus, PCl_3 has a trigonal pyramidal geometry.



SF_6

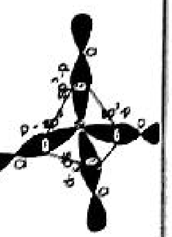
In SF_6, S is sp^3d^2-hybridized. S has six sp^3d^2-hybrid orbitals. Its hybrid orbitals overlap with p-orbitals of six flouri ne atoms to form six covalent bonds. Thus, SF_6 has an octahedral geometry.

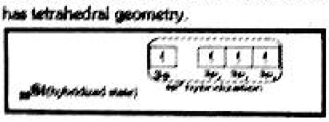




$SiCl_4$

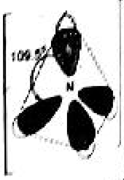
In $SiCl_4$, Si is sp^3-hybridized. Si has four sp^3-hybrid orbitals. Its hybrid orbitals overlap with p-orbitals of four chlorine atoms to form four covalent bonds. Thus, $SiCl_4$ has tetrahedral geometry.





NH_4^+

In NH_4^+, N is sp^3-hybridized. N has four sp^3-hybrid orbitals. Its hybrid orbitals overlap with s-orbitals of four hydrogen atoms to form three covalent bonds and one co-ordiante covalent bond. Thus, NH_4^+ has tetrahedral geometry.



Q14. (a) Define bond energy. Explain the various parameters which determine its strength.

(b) How do you compare the bond strengths of

(i) Polar and Non-polar molecules

Non-polar molecules are formed either between similar atoms (e.g., H_2) or have symmetrical structure (e.g., CCl_4). In H_2, the bond is non-polar while in CCl_4, individual bonds are polar. Generally, polar bonds are stronger than non-polar bonds.

Polar molecules have unsymmetrical structure. They always have polar bonds and polar bonds are stronger than non-polar bonds.

(ii) σ and π-bonds

	Sigma Bond		Pi Bond
1.	It is formed when two atomic orbitals overlap with their axes in a straight line.	1.	It is formed when two p-orbitals overlap with their axes parallel to each other.
2.	The overlap of atomic orbitals is more than pi bond. Hence, a large amount of energy is released and the bond is strong.	2.	The overlap of atomic orbitals is only slight. Hence, this bond is quite weak.
3.	The probability of finding electron is maximum around the line joining the two nuclei.	3.	The probability of finding electron is maximum above and below the line joining the two nuclei.
4.	A sigma bond is formed between the atoms, which are not already bonded.	4.	A Pi bond is formed between the atoms, which are already bonded by a sigma bond.
5.	Sigma bond is stronger than pi bond.	5.	Pi bond is weaker than sigma bond.
6.	Example: In Cl_2, there is sigma bond between two chlorine atoms. i.e. Cl – Cl	6.	Example: In O_2, there are two bonds between two oxygen atoms, one is sigma and other is pi. i.e. O = O

(c) Calculate the bond energy of H-Br. The bond energy of H-H is 436 kJmol⁻¹ and that of Br-Br is 193 kJmol⁻¹.

The H – H bond energy is 436 kJ/mol

i.e. $H + H \longrightarrow H_2 \qquad \Delta H = -436\ kJ/mol$

Thus

6.02×10^{23} bonds have energy $= 436\ kJ$

1 bond will have energy $= \dfrac{436}{6.02 \times 10^{23}} = 72.42 \times 10^{-23}\ kJ$

Since each hydrogen atom contribute equally, therefore, contribution of each hydrogen will be 36.21×10^{-23} kJ.

Similarly, Br – Br bond energy is 193 kJ/mol

and for one bond it is 32.06×10^{-23} kJ.

Thus, each Br atom will contribute 16.03×10^{-23} kJ.

Hence in case o H – Br, bond energy must be

$36.28 \times 10^{-23} + 16.03 \times 10^{-23} = 52.31 \times 10^{-23}$ kJ/molecule

Thus, for one mole it will be $52.31 \times 10^{-23} \times 6.02 \times 10^{23}$

$= 314.90$ kJ/mol.

Actual bond energy of HBr is 366 kJ/mol. This increase in bond energy is due to polar character of H – Br bond.

Q15. (a) Define dipole moment. How does it help to find out the shapes of molecules?

See Section 6.5.4

(b) The bond length of H-Br is 1.4×10^{-10}m. Its observed dipole moment is 0.79D. Find the percentage ionic character of the bond.

Unit positive charge = 1.6022×10^{-19} C and 1 D = 3.336×10^{-30} mC

Charge $= q = 1.6022 \times 10^{-19}$ C

Bond length $= r = 1.4 \times 10^{-10}$ m

$\mu_{obs} = 0.79$ D

$\mu_{ionic} = ?$

% ionic character= ?

$\mu_{ionic} = q \times r = 1.6022 \times 10^{-19}\ C \times 1.4 \times 10^{-10}$ m

$= 2.243 \times 10^{-29}$ mC

Since 1 D = 3.336×10^{-30} mC

Therefore

$$\mu_{ionic} = \frac{2.243 \times 10^{-29}}{3.336 \times 10^{-30}} = 6.723\text{D}$$

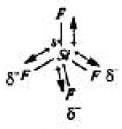
Thus $$\%\ \text{ionic character} = \frac{0.79}{6.723} \times 100 = 11.75\ \%$$

Q16. PF_3 is a polar molecular with dipole moment 1.02 D and thus the P-F bond is polar. Si, being in proximity of P in the Periodic table, it is expected that Si-F bond would also be polar but SiF_4 has no dipole moment. Explain why is it so?

PF_3 have a triangular pyramidal structure.

This structure is unsymmetrical. Thus in this structure individual bond moments do not cancel the effect of each other. Hence, it shows dipole moment.

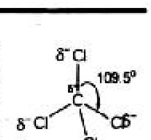
SiF_4 molecule has a regular tetrahedral structure. This structure is symmetrical. Thus in this structure individual bond moments cancel the effect of each other. Hence, SiF_4 does not show dipole moment.



Q17. Which of the following molecules will be polar or non-polar, sketch the structures and justify your answer.

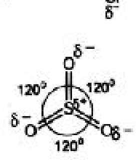
(i) CCl_4

In CCl_4, all C–Cl bonds are polar. CCl_4 molecule has a regular tetrahedral structure. This structure is symmetrical. It has uniform electron density distribution. In this structure, individual bond moments cancel the effect of each other. Therefore, its dipole moment is zero. Hence, in CCl_4, all C–Cl bonds are polar but molecule is overall non-polar.



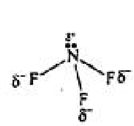
(ii) SO_3

In SO_3, all S=O bonds are polar. SO_3 molecule has a trigonal planar structure. This structure is symmetrical. It has uniform electron density distribution. In this structure, individual bond moments cancel the effect of each other. Therefore, its dipole moment is zero. Hence, in SO_3, all S=O bonds are polar but molecule is overall non-polar.



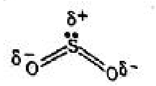
(iii) NF_3

In NF_3, all N–F bonds are polar. NF_3 molecule has a trigonal planar structure. This structure is not symmetrical. In this structure, individual bond moments do not cancel the effect of each other. Therefore, it has dipole moment. Hence, in NF_3, all N–F bonds are polar and molecule is also polar.



(iv) SO_2

In SO_2, both S=O bonds are polar. SO_2 molecule has an angular structure. This structure is not symmetrical. In this structure, individual bond moments do not cancel the effect of each other. Therefore, it has dipole moment. Hence, in SO_2, both S=O bonds are polar and molecule is also polar.



Q18. Explain the following:

(i) Bond distance is the compromise distance between two atoms.

(Gujranwala Board, 2009: Sargodha Board, 2010: D.G. Khan Board, 2011, 2012: Gujranwala Board, 2012)

See Section 6.1.2

(ii) In many cases, the distinction between a co-ordinate covalent bond and a covalent bond vanishes after bond formation in NH_4^+, H_3O^+ and $CH_3NH_3^+$. (Lahore Board, 2011)

A co-ordinate covalent bond is formed when both the shared electrons are donated by one of the atoms.

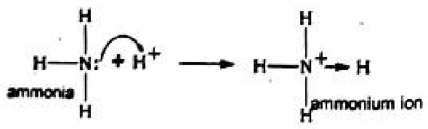
After bond formation in many cases no distinction remains between co-ordinate covalent bond and covalent bond.

Examples:

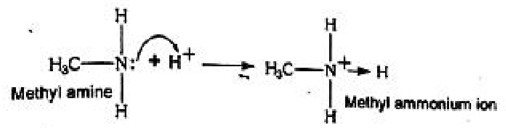
Formation of H_3O^+ ion

In H_3O^+ ion, experimentally it has been found that all bonds are equivalent. Thus, there is no distinction between co-ordinate covalent bond and covalent bond.

Formation of NH_4^+ ion is

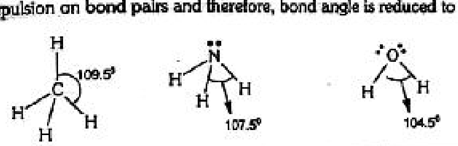


Formation of $CH_3NH_3^+$ ion is



(iii) The bond angles of H_2O and NH_3 are not 109.5° like that of CH_4. Although O- and N- atoms are sp^3 hybridized.

CH_4 molecule has no lone pair and its structure is tetrahedral with bond angles 109.5°. However, in NH_3 one lone pair is present which exerts repulsions on bond pairs thus the bond angle is reduced to 107.5°. In case of H_2O, two lone pairs are present which exert more repulsion on bond pairs and therefore, bond angle is reduced to 104.5°.



(iv) π-bond are more diffused than σ-bonds.

(Lahore Board, 2008, 2012, 2014: Bahawalpur Board, 2009: Multan Board, 2007, 2009, 2011: Sargodha Board, 2009: Faisalabad Board, 2007, 2010: D.G. Khan Board, 2010: Gujranwala Board, 2010, 2012, 2014: D.G. Khan Board, 2012: Rawalpindi Board, 2012: Rawalpindi Board, 2007, 2013)

σ-bond is formed by head on overlap of atomic orbitals of atoms. Therefore, electron density is largely present between the nuclei. However, π-bond is formed by sideways overlap of atomic orbitals. Therefore, electron density is largely present above and below the plane of nuclei. Hence π-bond is more diffused than σ-bond.

(v) The abnormality of bond length and bond strength in HI is less prominent than that of HCl.

(Lahore Board, 2007: D.G. Khan Board, 2011: Faisalabad Board, 2012: Rawalpindi Board, 2012)

In H-Cl, the electronegativity difference of H and Cl is 0.9.

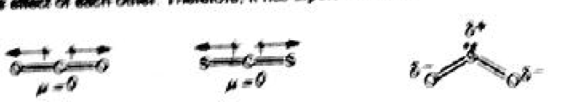
While in H-I, the electronegativity difference of H and I is less than 0.9

Due to greater electronegativity difference in H-Cl, the partial charges on H and Cl in HCl are greater than those on H and I in HI. As a result, H and Cl have more attractions and hence bond length and bond energy shows greater unexpected behaviour (abnormalities) than that of HI

(vi) The dipole moments of CO_2 and CS_2 are zero, but that of SO_2 is 1.61D.

(Gujranwala Board, 2009; Multan Board, 2010, 2012)

CO_2 and CS_2 have linear structures which are symmetrical. In these structures individual bond moments cancel the effect of each other. Hence, dipole moment becomes zero. However, SO_2 has bent or angular structure in which individual bond moments do not cancel the effect of each other. Therefore, it has dipole moment.



(vii) The melting and boiling points of electrovalent compounds (i.e. ionic compounds) are very high as compared with those of covalent compounds. Why?

Or Heat of vaporization and heat of sublimations (Lahore Board, 2012; Sargodha Board, 2014)

In ionic compounds ions are held together by strong electrostatic forces of attraction. A lot of energy is required to break these forces. Hence m.p. and b.p. of ionic compounds are very high.

While

In covalent compounds intermolecular forces are present in the form of dipole-dipole forces and H-bonding etc. These forces are easy to break than ionic forces. Hence covalent compounds have low m.p. and b.p. as compare to ionic compounds.

HELLO! Mr. Question here!

Multiple Choice Questions from PAST PAPERS

1. CsF has ionic character: **(Lahore board, 2014)**
   (a) 60% (b) 80% (c) 92% (d) 100%
2. The geometery of ethene is: **(Rawalpindi board, 2011)**
   (a) Tetrahedral (b) Trigonal planar (c) linear (d) V-shaped
3. Which molecule has zero dipole moment? **(Gujranwala board, 2013)**
   (a) NH_3 (b) $CHCl$ (c) HO_2 (d) BF_3
4. The number of electrons shared in SF_6 molecule is: **(Gujranwala board, 2010)**
   (a) 4 (b) 12 (c) 6 (d) 8
5. The amount of energy released by absorbing electron in the valence shell is: **(Gujranwala board, 2010)**
   (a) ionization energy (b) electron affinity
   (c) electronegativity (d) atomization energy
6. Formation of chemical bond takes places when **(Lahore board, 2013)**
   (a) energy is absorbed
   (b) forces of repulsion overcome forces of attraction
   (c) forces of attraction are equal to forces of repulsion
   (d) forces of attraction overcome forces of repulsics
7. Carbon dioxide and methane have dipole moment value: **(Gujranwala board, 2009)**
   (a) zero and 1.85 D (b) 1.70 D and 1.80 D
   (c) both have zero (d) none of these
8. Noble gases have maximum stability and least reactivity because **(Gujranwala board, 2009)**
   (a) they are very safe (b) their valence shells are complete
   (c) they are gases (d) they are present in zero group
9. Octet rule is not followed in the formation of: **(Bahawalpur Board, 2010; Faisalabad Board, 2011; Gujranwala board, 2009, 2012)**
   (a) NF_3 (b) CF_4 (c) CCl_4 (d) PCl_5
10. Ionic and co-ordinate covalent bonds are present in: **(Gujranwala board, 2011)**
    (a) SO_2 (b) NH_4Cl (c) C_2H_2 (d) H_2O
11. The highest electronegative element in the periodic table is: **(Gujranwala board, 2011)**
    (a) oxygen (b) nitrogen (c) chlorine (d) fluorine
12. According to VSERP theory, the shape of PH_3 molecule is:
    (a) Trigonal Pyramidal (b) Tetragonal (c) Linear (d) Trigonal Planar

13. *Mg* becomes Iso electronic with Neon when it: *(Multan Board, 2011)*
(a) Looses one electron (b) Looses two electrons
(c) Gains one electron (d) Gains two electrons

14. The radius of Na^{+1} ion is *(Rawalpindi board, 2013)*
(a) 92 pm (b) 93 pm (c) 94 pm (d) 95 pm

15. Bond order of O_2^{2-} is *(Rawalpindi board, 2013)*
(a) Zero (b) One (c) Two (d) Three

16. The dipole moment of SO_2 is: *(Multan Board, 2013)*
(a) 0.0 D (b) 0.12 D (c) 0.95 D (d) 0.78 D

17. Which one of the followings has the highest bond order? *(Multan Board, 2013)*
(a) O_2^{1+} (b) O_2^{+2} (c) O_2^{-1} (d) O_2^{-2}

18. The most stable elements are: *(Lahore Board, 2009)*
(a) Halogens (b) Lithium family (c) Noble gases (d) None of these

19. The hybridization of Carbon in C_2H_4 is: *(Lahore Board, 2009)*
(a) sp (b) sp^2 (c) sp^3 (d) Not Hybridized

20. The geometry of ethene is: *(Faisalabad Board, 2009)*
(a) Tetrahedra l (b) Trigonal Planar (c) Linear (d) V-shaped

21. The value of dipole moment of CS_2 is *(Bahawalpur Board, 2009)*
(a) 0.12D (b) Zero (c) 1.61D (d) 0.95D

22. The paramagnetic property of Oxygen is well explained on the basis of *(Sargodha Board, 2009, 2013)*
(a) VSERP theory (b) VB theory (c) MO theory (d) CF theory

23. The bond order of N_2 according to MO theory is: *(Sargodha Board, 2009)*
(a) zero (b) 1 (c) 2 (d) 3

24. The four equivalent sp^3 hybrid orbitals in space are at an angle of: *(D.G. Khan Board, 2009)*
(a) 120°C (b) 107.5°C (c) 104.5°C (d) 109.5°C

25. Bond angle between H – S – H bond is *(Lahore Board, 2010)*
(a) 104.5° (b) 107.5° (c) 92° (d) 95°

26. S.I unit of dipole moment is: *(Lahore Board, 2010)*
(a) pm (b) Debye (c) mc (d) all

27. Which pair has trigonal planar geometry? *(Faisalabad Board, 2010)*
(a) CO_2, SO_2 (b) NH_3, PH_3 (c) BF_3, AlH_3 (d) H_2O, C_2H_2

28. The decrease in atomic radius is small when we travel from left to righ in transition elements. Sc_{21} to Zn_{30}, Y_{39} to Cd_{48} due to: *(Faisalabad Board, 2010)*
(a) valence electrons (b) Intervening electrons

(c) Shielding effect (d) screening effect

29. Which of the following compound has a coordinate covalent bond? *(Sargodha Board, 2010)*
(a) NH_4Cl (b) NaCl (c) HCl (d) $ALCl_3$

30. The carbon atom in C_2H_4 is *(Sargodha Board, 2010)*
(a) sp^3 hybridized (b) sp^2 hybridized (c) sp hybridized (d) dsp^2 hybridized

31. MOT was proposed by *(Rawalpindi Board, 2010; D.G. Khan Board, 2011)*
(a) Mosley (b) Werner (c) Kossel (d) Mullikan's

32. Which of the following molecule has a coordinate covalent bond. *(D.G. Khan Board, 2010)*
(a) NH_3 (b) $AlCl_3$ (c) HCl (d) NH_4Cl

33. Total number of sigma bonds in ethyne (CH = CH) are *(D.G. Khan Board, 2010)*
(a) five (b) three (c) two (d) four

34. The SI unit of dipole moment is *(Lahore Board, 2011)*
(a) Joule (b) Debye (c) Coulometer (d) $N.m^{-2}$

35. Total number of bonds in C_2H_4 molecule are *(Lahore Board, 2011)*
(a) six (b) Four (c) Five (d) Eight

36. The most electronegative element is *(Faisalabad Board, 2011)*
(a) N_2 (b) F_2 (c) O_2 (d) H_2

37. Dipole moment of CO_2 is: *(Lahore Board, 2007)*
(a) 1.84 D (b) Zero D (c) 0.95 D (d) 2.2 D

38. In sp^2 hybridization, the orbitals are oriented at an angle of: *(Lahore Board, 2007)*
(a) 109.5° (b) 120° (c) 180° (d) 90°

39. The geometry of $BeCl_2$ is *(Faisalabad Board, 2007)*
(a) Linear (b) Planar trigonal (c) Tetrahedral (d) None of these

40. The molecule which cannot for co-ordinate covalent bond with H^+ ion is
(a) NH_3 (b) H_2O (c) PH_3 (d) CH_4

41. VSEPR theory was proposed by *(Sargodha Board, 2014)*
(a) Kossel (b) Lewis (c) Nylholm and Gillespie (d) Sidwick

42. The shielding effect is responsible for:
(a) The decrease in nuclear attractive influence over the valence electrons
(b) The increase in nuclear attractive influence over the valence electrons
(c) The decrease repulsion between Nucleus and Inner Electrons
(d) The increase in attraction between Nucleus and Inner Electrons

Answers to Multiple Choice Questions from Past Papers.									
Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(c)	2	(b)	3	(d)	4	(c)	5	(b)
6	(d)	7	(c)	8	(b)	9	(d)	10	(b)
11	(d)	12	(a)	13	(b)	14	(d)	15	(b)
16	(d)	17	(b)	18	(c)	19	(b)	20	(b)
21	(b)	22	(c)	23	(d)	24	(d)	25	(c)
26	(c)	27	(c)	28	(b)	29	(a)	30	(b)
31	(d)	32	(d)	33	(b)	34	(c)	35	(a)
36	(b)	37	(b)	38	(b)	39	(a)	40	(d)
41	(c)	42	(a)						

Detailed Explanation of Past Papers MCQs & answers to all Past Papers SHORT QUESTONS in COLLEGE CHEMISTRY OBJECTIVE BOOK-I

SHORT & LONG QUESTIONS FROM PAST PAPERS

OCTET RULE

Short Questions

(1) Explain Octet rule
(2) What is octet rule? Why certain elements do not obey it? **(Bahawalpur Board, 2010)**
(3) what is octet rule? Give two examples of compounds which deviate it. **(Multan Board, 2011: Lahore Board, 2007, 2012: Multan Board, 2012)**
(4) Write the Lewis structure of NH_4OH and H_2SO_4 **(Multan Board, 2012)**
(5) Write the Lewis structures of CS_2 and CCl_4 **(Sargodha Board, 2014)**

ATOMIC RADIUS, IONIC RADIUS

Short Questions

(1) Define atomic radius. How does it vary in groups and periods? **(Lahore Board, 2009)**
(2) Why atomic radius cannot be measured accurately (or precisely)? **(Sargodha Board, 2010: Gujranwala Board, 2010, 2014)**
(3) Why atomic radius increases down the group? **(Rawalpindi Board, 2007: Sargodha Board, 2009: Multan Board, 2010)**
(4) Why ionic radius of a cation (positive ion) is smaller than its parent atom? **(Lahore Board, 2009: OR** The radius of cation is smaller than atomic radius but that of an anion is greater than atomic radius. **(Multan Board, 2011: Lahore Board, 2010, 2014)**
(5) Anionic radius is always larger than parent atom. Why? **(Sargodha Board, 2007) OR** Why the ionic radius of Cl^- ion increases from 99 pm to 181 pm? **(Lahore Board, 2013) OR**

Compare the radius of chloride ion with its parent atom. Give reasons. **(Gujranwala Board, 2008**
(6) What is interionic distance? Explain with example. **(D.G. Khan Board, 2010)**
(7) Write short note on atomic and ionic radii. Give examples.

IONIZATION ENERGY

Short Questions

(1) Define ionization energy. What factors influence the ionization energy/potential? **(Lahore Board, 2010, 201*)**
(2) Why the ionization energies values decrease down the group although necular charge increases. **(Faisalabad Board, 2008: D.G. Khan Board, 2008: Bahawalpur Board, 2009, 2011: D.G. Khan Board, 2009, 2012: Sargodha Board, 2012: Gujranwala Board, 2013) of Group VI A etc.**
(3) Why ionization energy increases from left to right in periods? **(D.G. Khan Board, 2007: Rawalpindi Board, 2009)**
(4) Define ionization energy/potential. How does it vary (or trend) in periodic table? **(Gujranwala Board, 2008: Multan Board, 2009, 2011, 2012: Sargodha Board, 2010: Faisalabad Board, 2007, 2012, 2013: D.G. Khan Board, 2011, 2012: Bahawalpur Board, 2012: Lahore Board, 2013, 2014)**
(5) Define ionization energy. Why second ionization energy/potential of an element is always greater than first ionization energy/potential? **(Lahore Board, 2008: Bahawalpur Board, 2008: Bahawalpur Board, 2010)**
(6) 1st ionization energy of Mg is lower than its 2nd ionization energy. Explain **(Rawalpindi Board, 2011)**
(7) Explain that ionization energy is the index of metallic character. **(D.G. Khan Board, 2009: Sargodha Board, 2013)**
(8) Orbital nature also affect the ionization energy. Explain. **(D.G. Khan Board, 2010)**

Long Questions

(1) Define ionizaiton energy. Give factors upon which it depends. How does it vary in periodic table? **(Rawalpindi Board 2009: Multan Board, 2012)**

ELECTRON AFFINITY

Short Questions

(1) Define electron affinity. Discuss its trent in periodic table. **(Azad Kashmir Board, 2012) OR** How do electron affinity values vary in the periodic table? **(Multan Board, 2010)**
(2) Why the first electron affinity for most of the elments is negative while the second electron affinity for all the elements is positive. **(D.G. Khan Board, 2008: (Lahore Board, 2008: Sargodha Board, 2009) OR** Why the second electron affinity of oxygen is positive? **(Bahawalpur Board, 2008)**
(3) What factors influence the electron affinity? **(Faisalabad Board, 2011)**
(4) Define electron affinity. Name the factors affecting it. How does it vary in the periodic table? **(Lahore Board, 2013)**

ELECTRONEGATIVITY

Short Questions

(1) Define (a) electronegativity (b) electron affinity **(Bahawalpur Board, 2011)**
(2) What is electronegativity? Give the names of most and the least electronegative elements. **(Gujranwala Board, 2010)**

(3) Define electronegativity. How do electronegativity values vary in the periodic table? (Bahawalpur Board, 2008, 2012: Faisalabad Board, 2009: Faisalabad Board, 2010: Rawalpindi Board, 2010, 2011: D.G. Khan Board, 2012: Azad Kashmir Board, 2012: Multan Board, 2007, 2013: Lahore Board, 2010) OR Define electronegativity. Give its trend in periodic table. (Faisalabad Board, 2011)

(4) How electronegativity values of elements help us in undrestanding the nature of chemical bond? (Faisalabad Board, 2013) OR How does the electronegtivity difference decide the nature of chemical bond? (Lahore Board, 2007)

Long Questions

(1) What is electronegativity? Discuss its variation in the perioidc table. How does it effect the bond strength. (Sargodha Board, 2009: D.G. Khan Board, 2012)

(2) Define the term electronegativity. Discuss its variation in the periodic table. (Faisalabad Board, 2011)

IONIC BOND, COVALENT BOND, COORDINATE COVALENT BOND

Short Questions

(1) Why the covalent bonds are directional? (Multan Board, 2008)

(2) Separate the following molecules as polar or non-polar. (Gujranwala Board, 2013)
(i) CO_2 (ii) CH_3OH (iii) CCl_4 (iv) HF

(3) No bond in chemistry is 100% ionic. Justify it. (Faisalabad Board, 2007)

(4) Define ionic bond. Give one example. (Azad Kashmir Board, 2012)

(5) What is non-polar covalent bond? Give an example. (Multan Board, 2009)

(6) Define polar covalent bond with example. (Faisalabad Board, 2009: Sargodha Board, 2011)

(7) Tell the number of electron pairs shared in CH_3Cl and how many bonds are polar? (Bahawalpur Board, 2011)

(8) Define coordinate covalent bond and give its two examples (Gujranwala Board, 20.. Sargodha Board, 2010: Faisalabad Board, 2011: Rawalpindi Board, 2011: Bahawalpur Board, 20.. Multan Board, 2007, 2013: Sargodha Board, 2013: Lahore Board, 2014)

(9) Explain the limitation of Lewis model. (D.G. Khan Board, 2011)

(10) How a coordinate covalent bond differs from covalent bond? (Lahore Board, 2013)

Long Questions

Differentiate between covalent and co-cordinate covalent bonds with two examples in each case. (Bahawalpur Board, 2011)

VALENCE SHELL ELECTRON PAIR REPULSION THEORY

Short Questions

(1) Write down two postulates of VSEPR theory. (Lahore Board, 2010: Multan Board, 2012)

(2) Write the order of repulsion between electron pairs according to VSEPR-Theory (Gujranwala Board, 2012)

(3) Why the lone pairs of electrons on an atom occupy more space? (Rawalpindi Board, 20.. Lahore Board, 2009: Rawalpindi Board, 2011: Sargodha Board, 2013)

(4) Why repulsive forces are less between lone pairs than bond pairs? (Rawalpindi Board, 20.. Sargodha Board, 2014)

(5) What is the basic assumption of VSEPR theory, and discuss the shape of a molecule (BF_3) containing three electron pairs? (Lahore Board, 2013: Rawalpindi Board, 2013) NOTE BF_3 molecule is on page

(6) Why the molecule of BF_3 is triangular planar? (D.G. Khan Board, 2008)

(7) Draw and explain the geometry of NH_3 molecule according to valence shell electron pair repulsion theory. (Faisalabad Board, 2013)

(8) NH_3 and NF_3 have different bond angles. Justify. (Gujranwala Board, 2014) OR In NH_3 the bond angle is 107.5° while in NF_3 the bond angle is 102° (Bahawalpur Board, 2011)

Long Questions

(1) Give three postulates of VSERP theory. Also discuss the struture of $BeCl_2$ in the light of this theory? (D.G. Khan Board, 2009)

(2) Write the postulates of VSEPR theory and discuss the structure of NH_3 with reference to this theory. (Sargodha Board, 2010)

(3) Explain VSEPR theory. Discuss structure of SO_3 according to this theory. (D.G. Khan Board, 2010)

(4) Discuss with two suitable example VSEPR theory of covalent bond. (Lahore Board, 2007)

(5) Write the main postulates of VSERP theory and explain the structure of ammonia on the basis of this theory. (Lahore Board, 2012)

(6) Write down the essential features of VSEPER theory. Also discuss the cases of water and ammonia molecules. (Sargodha board, 2007)

(7) Write the postulates of VSEPR theory and discuss the structure of methane with reference to VSEPR theory. (Multan Board, 2007)

(8) Give important postulates of VSEPR theory (Gujranwala Board, 2014: Sargodha Board, 2012, 2014)

(9) Explain VSEPR theory with suitable examples. (Bahawalpur Board, 2012)

VALNCE BOND THEORY, HYBRIDIZATIN

Short Questions

(1) Write two points of Valence Bond Theory. (Gujranwala Board, 2011)

(2) Sigma bonds are more stronger than pi bond. Why? (Rawalpindi Board, 2007: D.G. Khan Board, 2007: Faisalabad Board, 2009: Gujranwala Board, 2011: Sargodha Board, 2011, 2012, 2013) OR Why pi bond is weaker than sigma bond? (Gujranwala Board, 2009)

(3) Define orbital hybridization and overlapping of orbitals. (Rawalpindi Board, 2013)

(4) The bond anlgels of H_2O and NH_3 are not 109.5° like that of CH_4, although oxygen and nitrogen atoms are sp^3-hybridized. Why? (Gujranwala Board, 2009: Lahore Board, 2009, 2013: Bahawalpur Board, 2009: Sargodha Board, 2012: Rawalpindi Board, 2012: Multan Board, 2012) OR OR Bond angles of CH_4, NH_3 and H_2O are different although all have sp^3 hybridization.Justify it. (Sargodha Board, 2014)

(5) Deviation in bond angle in water (H_2O) molecule is more than in ammonia (NH_3) molecule although both have tetrahedral structures. (Gujranwala Board, 2012)

(6) What type of hybridization takes place in boron trifluoride molecule? Comment on it. (Gujranwala Board, 2008)

Long Questions

(1) Explain valence bond theory (VBT) with examples showing the overlapping of different orbitals. (D.G. Khan Board, 2012)

(2) What is orbital hybridization? Explain the structure of CH_4 on the basis of sp^3 hybridization. (Faisalabad Board, 2009: Lahore Board, 2014)

(3) Define Hybridization. Classify it and discuss the structure of ethene ($CH_2 = CH_2$) (sp^2 hybridization) (Multan Board, 2010, 2011: Gujranwala Board, 2011, 2013)

(4) Define atomic orbital hybridization. With its help how we can describe the geometries of H_2O and NH_3? (Rawalpindi Board, 2010) OR What is orbital hybridization? Explain sp^3 hybridization with two examples. (Gujranwala Board, 2008: D.G. Khan Board, 2011: Multan Board, 2013: Sargodha Board, 2013)

(5) Write a note on sp hybridization with an example of acetylene. (Azad Kashmir Board, 2012)

(6) Define and classify atomic orbital hybridization. Discuss the structure of BF_3 in the light of orbital hybridization. (Faisalabad Board, 2007)

(7) Define sp^2 hybridization and on its basis explain the structure of ethene. (Faisalabad Board, 2013)

MOLECULAR ORBITAL THEORY

Short Questions

(1) How molecular orbital theory justifies that Helium atoms cannot make the He_2 (Faisalabad Board, 2008: Multan Board, 2008: Sargodha Board, 2009, 2013) OR How molecular orbital theory explains that helium is monoatomic? (Faisalabad Board, 2010 OR Draw diagram of He-molecule according to MOT. Also give its bond order. (Multan Board, 2013) OR He_2 molecule is not formed. Why? (Multan Board, 2007)

(2) Give the sequence of molecular orbitals in N_2 molecule. (Bahawalpur Board, 2008: Multan Board, 2010)

(3) Why MOT is superior to VBT? (Multan Board, 2009: D.G. Khan Board, 2010: Lahore Board, 2011: Sargodha Board, 2011: Gujranwala Board, 2011: Multan Board, 2013)

(4) Why nitrogen molecule is diamagnetic? (Gujranwala Board, 2010)

(5) Helium is diamagnetic in nature. Justify? (Lahore Board, 2011)

(6) Define bond order. Mention bond order of N_2 molecule. (D.G. Khan Board, 2012)

(7) Define (or Explain) bond order. Calculate the bond order of nitrogen (or hydrogen etc.) molecule. (Sargodha Board, 2007: Lahore Board, 2007: Azad Kashmir Board, 2012: Lahore Board, 2014)

(8) Define bond order and what is bond order of O_2^{2+} ? (Faisalabad Board, 2013)

(9) Why MOT is suprior both VSEPR and VBT? (Sargodha Board, 2013)

(10) Sketch the molecular orbital picture of O_2. (Gujranwala Board, 2013)

(11) What is bond order? How it can be calculated? (D.G. Khan Board, 2007)

(12) Why the energy of antibonding molecular orbital is higher than corresponding bonding molecular orbitals? (Sargodha Board, 2007: Lahore Board, 2013)

(13) Differentiate between bonding and antibonding molecular orbitals. (Lahore Board, 2008: D.G. Khan Board, 2012)

Long Questions

(1) Explain the molecular orbital structures of following molecules on the basis of the MOT:
(i) N_2 (Nitrogen) (ii) O_2 (oxygen) (Lahore Board, 2013)

(2) Explain paramagnetic nature of oxygen on the basis of molecular orbital theory. (Bahawalpur Board, 2009: D.G. Khan board, 2007: Gujranwala Board, 2010: Lahore Board, 2011, 2014)

(3) Describe the bonding in O_2 according to molecular orbital theory and explain its paramagnetic property. (Lahore Board, 2014)

(4) Explain the Molecular Orbital Theory. Give the molecular orbitals configuratio and structure of O_2 (Multan Board, 2012)

(5) What is the basis of molecular orbital theory and explain paramagnetic nature of oxygen (Gujranwala Board, 2009)

BOND LENGTH, BOND ENERGY

Short Questions

(1) Why a double bond is stronger than single bond? (Rawalpindi Board, 2009)

(2) Define (a) electronegativity (b) bond energy

(3) Compare bond strength of polar and non-polar bonds. (Rawalpindi Board, 2010: Multan Board, 2013)

(4) Define bond length and bond energy. (Faisalabad Board, 2007, 2012: Sargodha Board, 2012)

(5) Define bond energy with two parameters which determine its strength. (Gujranwala Board, 2013)

Long Questions

Define bond energy. Discuss two factors effecting the bond energy (Lahore Board, 2010)

Define bond energy and explain the various parameters which determine its strength. (Faisalabad Board, 2012)

Define bond energy and explain with the help of a suitable example the effect of ionic character on its value. (Sargodha Board, 2013)

DIPOLE MOMENT

Short Questions

(1) Why the dipole moment of CO_2 is zero and that of H_2O is 1.85D. (Faisalabad Board, 2008: Multan Board, 2008)

(2) Why the dipole moment of CO_2 and CS_2) is zero and that of SO_2 is 1.61D. (Lahore Board, 2013)

(3) Why the dipole moment of CH_4 is zero? (Multan Board, 2008)

(4) How the %age ionic character of the polar bond can be determined? (D.G. Khan Board, 2008) Bahawalpur Board, 2010: Sargodha Board, 2011: Bahawalpur Board, 2012)

(5) Dipole moment of CO is 0.12D but that of CO_2 is zero. Why? (Faisalabad Board, 2009)

(6) Define (or What is) dipole moment. Give its various units (or S.I. units). (D.G. Khan Board, 2007, 2009: Rawalpindi Board, 2009, 2010: Lahore Board, 2012: Multan Board, 2012: Sargodha Board, 2007, 2013)

(7) Define dipole moment. Give its mathematical expression. (Rawalpindi Board, 2012: Sargodha Board, 2013)

(8) CO_2 is a non-polar molecule although its bonds are polar. Why? (Gujranwala Board, 2008)

(9) CO_2 molecules have linear structure while H_2O have angular structure. Comment. (Gujranwala Board, 2011)

(10) Why the dipole moment of SO_2 is 1.61 D but that of SO_3 is zero? (Lahore Board, 2013)

(11) Why CS_2 molecule is linear while SO_2 molecule is angular? (D.G. Khan Board, 2012)

Long Questions

(1) What are dipole moments. Give its SI units. How does it explain the geometry of CO_2 and BF_3 molecules. (Lahore Board, 2009)

(2) *What is Dipole Moment? Give its various units. How does it help to find out the shapes of Molecules?* **(Multan Board, 2009)**

(3) *What is dipole moment. Give its units. Explain the structure of CO_2 and H_2O on the basis of dipole moment.* **(Rawalpindi board 2007: Faisalabad Board 2010)**

(4) *What is Dipole moment? What information does it provide. Explain with examples.* **(Bahawalpur Board, 2010)**

(5) *What is Dipole Moment? Give its various units.Also give its significance?* **(Sargodha Board, 2011)**

TEST YOUR SKILLS

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) The shape of the NF_3 molecule is
(a) square planar (b) tetrahedral (c) Triangular planar (d) Triangular pyramidal

(ii) Which of the following is the strongest bond?
(a) Ionic (b) covalent (c) hydrogen (d) van der Waal

(iii) In which of the following molecules, the central atom uses sp^2 hybrid atomic orbitals in forming bonds?
(a) ethane (b) ethene (c) NH_3 (d) ethyne

(iv) Which of the following geometrical configuration corresponds to sp^2 hybridization?
(a) tetrahedral (b) pentagonal bipyramid (c) triangular planar (d) octahedral

(v) The Carbon atoms in C_2H_4 is
(a) sp^3 hybridized (b) sp^2 hybridized (c) sp hybridized (d) dsp^2 hybridized

(vi) Noble gases have maximum stability and least reactivity because
(a) they are very safe (b) their valence shells are complete
(c) they are gases (d) they are present in zero group

(vii) Ionic reactions are
(a) fast (b) slow (c) very slow (d) none

(viii) Covalent compounds are soluble in
(a) polar solvents (b) non-polar solvents (c) concentrated acids (b) all solvents

(ix) An sp^3 hybrid orbital contains
(a) 1/4 s character (b) 1/2 s character (c) 2/3 s character (d) 3/4 s character

(x) A molecular orbital can contain maximum electron equal to
(a) One (b) two (c) Three (d) Four

(xi) Shielding effect of inner electrons causes
(a)decrease in atomic radii in a period (b) increase in atomic radii in a period
(c) decrease in atomic radii down the group (d) increase in atomic radii down the group

(xii) The molecule which can not form co-ordinate covalent bond with H^+ ion is
(a) NH_3 (b) H_2O (c) PH_3 (d) CH_4

(xiii) The polarity of a covalent bond depends upon
(a) difference in ionization energies of bonded atoms
(b) difference in electron affinities of bonded atoms
(c) difference in atomic radii of the bonded atoms
(d) differences in electronegativity of bonded atoms

(xiv) Which of the following molecules have multiple bonds
(a) CH_4 (b) C_2H_4 (c) C_2H_6 (d) CCl_4

(xv) Which of the following compound has a coordinate covalent bond?
(a) NH_4Cl (b) NaCl (c) HCl (d) $AlCl_3$

(xvi) The geometry of NH_4^+ ion is
(a) square planar (b) tetrahedral (c) trigonal planar (d) linear

(xvii) Carbon dioxide and methane have dipole moment value
(a) zero and 1.85 D (b) 1.70 D and 1.80 D (c) both have zero (d)none of these

SUBJECTIVE

Time: 2:10 Hours **Marks: 68**

Note: Out of Questions 2,3 and 4. Write any TWENTY TWO(22) short answers. While writing answers write question numbers carefully. **(22x 2)=44**

Section - I

Q2. Answer any Eight parts from the followings.

(i) BF_3 has zero dipole moment. Why?
(ii) What is dipole moment. Give its mathematical form and SI units?
(iii) In N_2 molecules, $\sigma 2p_x$ is of higher energy than $\pi 2p_y$ and $\pi 2p_z$. Why?
(iv) Differentiate between sigma and pi bond.
(v) How does carbon atom get the energy for excitation of its electron from 2s to 2p orbital?
(vi) The distinction between covalent bond and co-ordinate covalent bond is finished. Give example.
(vii) Ionization energy increases from left to right in a periodic table. why?
(viii) Fluorine has less electron affinity than Cl. Why?
(ix) In NF_3 the bond angles are shorter than NH_3. Why?
(x) Atomic radii decreases from left to right in a periodic table. Why?
(xi) Ionic reactions are very fast. Why?
(xii) Size of trivalent ion is smaller than divalent ion. why?

Q3. Answer any Eight parts from the followings.

(i) Why noble gases are most stable?
(ii) What is the meaning of compromise distance in bond formation?
(iii) Atomic radii decrease in a period and increase down a group. Why?
(iv) Why M.O.T is superior to V.B.T?
(v) Ionization energy decreases down a group. Why?
(vi) What happens to the energy when electron is added to an atom to form an anion?
(vii) How does electronegativity tells about the nature of bond?
(viii) What is the trend of atomic radii in trasition metals?
(ix) Why electron is transferred form elements with low ionization energy to elements with high electron affinity?
(x) Why atomic radius can not be measured accurately?
(xi) How ammonia molecule forms a coordinate covalent bond?
(xii) Orbital hybridization explains valence of certain elements. How?

Q4. Answer any Six parts from the followings.

(i) Lone pair of electrons occupies more space than bond pair. Why?
(ii) What is bond order and how is it calculated?
(iii) How does bond length depend upon hybridization?
(iv) H – F is the most polar while H – I is the least polar. Why?
(v) Dipole moment of CO_2 is zero but that of H_2O is 1.85, although both are triatomic. Why?
(vi) The radius of anion is always larger than parent atom. Why?
(vii) Bond distance is the compromise distance between two atoms. Explain with reason?
(viii) Why sodium chloride is insoluble in benzene, but soluble in water?
(ix) Differentiate between paramagnetism and diamagnetism?

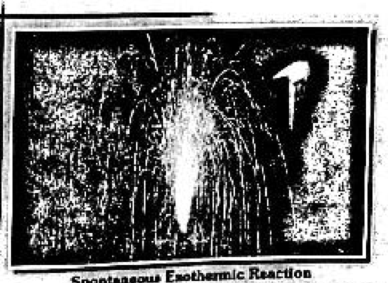
Section – II (Attempt any three questions) (8x 3)=24

Q5. (a) Explain paramagnetic nature of O_2 molecules on the basis of MOT.
(b) What is orbital hybridization? Explain sp hybridization with reference to ethyne. (04)
Q6. (a) How dipole moment can be used to decide the shapes of molecules? (04)
(b) Predict the shapes of following g molecules on the basis of VSEPR theory. (04)
(i) NF_3 (ii) SO_2 (iii) PCl_5 (iv) NH_3 (04)
Q7. (a) What is octet rule?
(b) Define electron affinity. How does it very in periodic table? (02)
(c) What is relationship of bond energy with ionic character of covalent bond? (03)
Q8. (a) What is co-ordinate covalent bond? Give examples. (03)
(b) The bond length of H-Br is 1.4×10^{-10}m. Its observed dipole moment is 0.79D. (04)
Find the percentage ionic character of the bond.
Q9. (a) When a second electron enters in a uninegative ion, energy is absorbed. Explain why? (04)
(b) How the bonding in the following molecules can be explained with respect to valance bond theory? (02)
(i) O_2 molecule (ii) N_2 molecule (iii) H_2S molecule (03)
(c) Write the postulates of VSEPR theory and discuss the structure of NH_3 with reference to this theory. (03)

Chapter 7

THERMOCHEMISTRY

G.H. Hess



Spontaneous Exothermic Reaction

CONTENTS

Chapter-7 Thermochhemistry

INTRODUCTION

Thermodynamics

The branch of science, which deals with energy changes, is known as thermodynamics.

Thermochemistry

The branch of chemistry which deals with energy changes in a chemical reaction is called thermochemistry.

Why heat is evolved or absorbed in a chemical reaction?

- During chemical reaction, bond breaking and making takes place.
- Bond breaking absorbs energy and bond making releases it.
- In chemical reaction, energy required to break bonds is not equal to the energy evolved for bond making. Different substances have different energies and thus total energy of reactants is always different from the total energy of products.
- This difference of energy is either evolved or absorbed during a chemical reaction. This is called heat of reaction.

TYPES OF REACTIONS

On the basis of absorption or evolution of heat, reactions are classified as

(i) Exothermic reactions.

(ii) Endothermic reactions.

EXOTHERMIC REACTIONS

The reactions in which heat is evolved are known as exothermic reactions.

- In such reactions, total energy of the products is less than the total energy of the reactants. This difference of energy is evolved as heat.
- The heat is given out and temperature of the system rises above the room temperature.
- After some time heat is lost to the surroundings and temperature falls to room temperature.
- The evolved heat of reaction is indicated by negative sign.

Examples:

(i) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393.7$ kJ/mol

(ii) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H = -285.58$ kJ/mol

(iii) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$ $\Delta H = -41.6$ kJ/mol

ENDOTHERMIC REACTIONS

The reactions in which heat is absorbed are known as endothermic reactions.

In such reactions total energy of the products is greater than the total energy of the reactants. This difference of energy is absorbed as heat. Thus, heat required for reaction is obtained from reactants and thus temperature of the system falls below the room temperature. After some time heat is absorbed from surrounding and temperature again rises to room temperature.

The absorbed heat of reaction is indicated by positive sign.

Examples:

$H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$ $\Delta H = +52.96$ kJ/mol

$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$ $\Delta H = +180.51$ kJ/mol

Difference between Exothermic and Endothermic reactions.

	Exothermic Reactions		Endothermic Reactions
1	The reactions in which heat is evolved are known as exothermic reactions.	1	The reactions in which heat is absorbed are known as endothermic reactions.
2	In these, total energy of the product is less than that of reactant.	2	In these, total energy of the product is more than that of reactant.
3	In these, temperature first rise then fall to room temperature	3	In these, temperature first fall then rise to room temperature.
4	The heat released is indicated by negative sign.	4	The heat absorbed is indicated by positive sign.
5	*Example:* $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393.7$ kJ/mol	5	*Example:* $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$ $\Delta H = +180.51$ kJ/mol

Importance and Limitations of Thermochemistry

- Thermochemistry tells about the energy or heat contents of the system including reactions. This knowledge is used to explain chemical bonding and chemical equilibrium.
- However, heat of reaction can be accurately determined only for few reactions. Thus, it limits the scope of thermochemistry.

SPONTANEOUS AND NON SPONTANEOUS REACTIONS

Exercise Q6. (a):

What are spontaneous and non-spontaneous processes? Give examples.

SPONTANEOUS REACTIONS

A process which takes place on its own without external help and move from non-equilibrium state to equilibrium state is called a spontaneous or natural process.

- It is a natural real process, therefore, it is unidirectional and irreversible process.

Examples

1. Water flows from higher level to lower level
2. Neutralization of a strong acid with a strong base

   $NaOH_{(aq)} + HCl_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O_{(l)}$
3. Reaction of Zn with $CuSO_4$ solution

   $Zn_{(s)} + CuSO_{4(aq)} \longrightarrow ZnSO_{4(aq)} + Cu_{(s)}$

In this reaction, blue colour of $CuSO_4$ solution disappears due to redox reaction.

- Some spontaneous reaction requires a small input of energy to start. But once they are started they go on by itself until complete.

  e.g. Burning of coal and hydrocarbons in air.
- Coal does not react with Both N_2 and O_2 are present in atomosphere. But they do not react. This reaction takes place, when energy is provided by lightning.air by itself. This reaction is started by a spark, when coal starts burning the reaction goes to completion by itself.

NON-SPONTANEOUS REACTIONS

A process which does not take place on its own is called a non-spontaneous process.

- It does not occur in nature. It is reverse of spontaneous process.
- Some non-spontaneous processes can be made spontaneous by continuous supply of energy from external source.

Examples:

1. Pumping of water uphill
2. Transfer of heat from cold interior part of refrigerator to the hot surroundings.
3. Reaction of N_2 with O_2 to form NO

   $N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$

Both N_2 and O_2 are present in atmosphere. But they do not react. This reaction takes place, when energy is provided by lightning bolt.

Reversible reaction are intermediate between spontaneous and non - spontaneous process.

CRITERION FOR SPONTANEITY OF REACTION

Experience shows that spontaneous processes occur by the decrease of energy and heat is transferred to the surrounding. Thus it can be said that all exothermic reaction are spontaneous. However, there are many endothermic reactions, which are spontaneous.

$$H_2O_{(s)} \longrightarrow H_2O_{(l)} \quad \Delta H = 44 \text{ kJ/mol}$$

$$NH_4Cl_{(s)} \longrightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)} \quad \Delta H = 15.1 \text{ kJ/mol}$$

Hence energy change is not a criterion for spontaneity of reaction.

Spontaneity of reaction is actually judged by the free energy change in terms of entropy of system.

Difference between Spontaneous and Non-Spontaneous Processes

	Spontaneous Process		Non-Spontaneous Process
1	A process which takes place on its own without external help and move from non-equilibrium state to equilibrium state is called a spontaneous or natural process.	1	A process which does not take place on its own is called a non-spontaneous process.
2	It is a natural real process	2	It usually does not occur in nature.
3	It is unidirectional and irreversible process.	3	Some non-spontaneous processes can be made spontaneous by continuous supply of energy from external source
5	*Example:* (i) Water flows from higher level to lower level (ii) $NaOH + HCl \rightarrow NaCl + H_2O$	5	*Example:* (i) Pumping of water uphill (ii) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$

SYSTEM, SURROUNDING AND STATE FUNCTION

SYSTEM

Any real or imaginary part of the universe that is under study is called system.

A chemical system is usually a substance undergoing a chemical change.

SURROUNDING

Everything that is not part of the system is called surrounding.

BOUNDARY

The real or imaginary surface separating the system from surrounding is called boundary.

Examples

1. In experimental work, a specific amount of one or more substances forms a system e.g. 1 mole of O_2 in a cylinder fitted with a piston is a system. The piston, the cylinder and all other objects outside cylinder are surroundings.
2. Water contained in a cup is a system and the cup, air around it and the table on which it is present are all surroundings.
3. If reaction between Zn and $CuSO_4$ solution is taking place in a flask as shown in figure, the contents of flask is a system while flask and air around it is surrounding.

STATE

The condition of a system is called a state

When a process occurs, the state of system is changed.

Explanation

Consider a water system at a given T and V. This initial condition of water is called initial state. Now if water is heated in a beaker, its condition will be changed. The final condition of the system is called final state.

A comparison of final and initial state tells us about the change taking place in a system.

Example:

Let T_1 and T_2 are the temperatures at initial and final state of the water system then change in temperature (change in state) will be

$$\Delta T = T_2 - T_1$$

STATE FUNCTION

It is a macroscopic property of system which has definite values for initial and final states and it is independent of the path through which change take place.

Conventionally, capital letters are used to represent a state function.

Examples: Volume (V), Temperature (T), Enthalpy (H), Internal Energy (E) etc.

Let initial volume of gas is V_1. Its volume can be changed to V_2 by changing temperature or pressure. The change in volume is given by

$$\Delta V = V_2 - V_1$$

This change can be brought about by changing pressure or temperature.

Since V is a state function, therefore, ΔV is independent of the path through which change takes place (i.e. by changing T or P)

INTERNAL ENERGY

It is the sum of all the energies of all the particles (i.e., atom, ions and molecules) within a system.

It is denoted by 'E'. It depends upon kinetic and potential energy of the system.

i.e. E = K.E. + P.E.

Kinetic Energy

It depends upon the motion of molecules (i.e., translational, vibrational, rotational).

Potential Energy:

It is due to binding forces between the particles. It includes intramolecular forces such as covalent bond and intermolecular forces such as van der Waal's forces.

Facts

- Internal energy is a state function i.e., it depends only on the initial and final state of a system and not on the path through which change takes place.
- The internal energy of a system cannot be determined. Only changes in internal energy, denoted by ΔE, can be determined

  i.e., $\Delta E = E_2 - E_1$

ENERGY TRANSFER BETWEEN SYSTEM AND SURROUNDINGS:

WORK AND HEAT

When a system undergoes a change, energy is transferred into or out of the system in two fundamental ways i.e.; heat and work.

WORK

Work is a form of energy and is defined as the product of force and distance.

Work = Force × Distance

It is denoted by w. It is not the property of system. Hence, it is path function. It is not a state function.

Sign Convention for w

Work done by the system is negative i.e. – w

Work done on the system is positive i.e. +w

Units of w

The SI unit of work is Joule (J).

Other unit is erg

$1\ \text{erg} = 10^{-7}\ \text{J}$

There are many types of work.

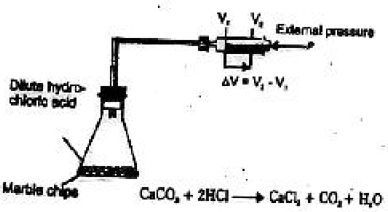
Chemical work

In chemistry most common type of work is pressure-volume work

Consider the reaction between $CaCO_3$ and HCl as shown in fig. The CO_2 produced change the volume form V_1 to V_2 against constant pressure 'P'. So, the pressure-volume work is given by

$$w = -P\Delta V$$

where, P = External pressure, ΔV = Change in volume



HEAT

It is the quantity of energy that flows across the boundary of a system during a change in state, due to the difference in T between system and surroundings.

It is denoted by q.

It is not the property of system. Hence, it is path function, it is not a state function.

Sign convention for q.

Heat gained by the system is positive i.e. +q

Heat lost by the system is negative i.e. – q

Units of q.

The SI unit of heat is joule (J).

Other unit is calorie (cal).

1 cal = 4.184 J

Exercise Q7.

(a) What is the first law of thermodynamics? How does it explain that (i) $q_v = \Delta E$ (ii) $q_p = \Delta H$

FIRST LAW OF THERMODYNAMICS

The law of conservation of energy is also called the first law of thermodynamics. It states,

Energy can neither be created nor destroyed although it can be changed form one form to another form.

OR ***The energy of the system and surrounding is conserved.***

Explanation

A system cannot destroy or create energy. However, it can exchange energy with its surroundings in the form of heat and work.

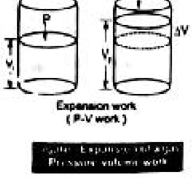
Consider a gas enclosed in a cylinder having a piston. If some heat 'q' is added to a system & some work 'w' is done on it then its internal energy is changed from 'E_1' to 'E_2'. The energy change is equal to the sum of both heat & work so that total energy of the system & surroundings remains constant. Hence, the mathematical form of first law of thermodynamics is

i.e; $\Delta E = E_2 - E_1 = q + w$ ______ (1)

ΔE = change in internal energy of system.

q = heat added to the system;

w = work done on the system.



Expansion work
(P-V work)

Figure: Expansion of a gas
Pressure volume work

Sign Conventions

ΔE is negative when system loses energy i.e. $-\Delta E$

ΔE is positive when system gains energy i.e; $+\Delta E$

Work done on the system is positive i.e; + w

Work done by the system is negative i.e; − w

Heat gained by the system is positive i.e; + q

Heat lost by the system is negative i.e; − q

HEAT CHANGES AT CONSTANT VOLUME

At constant volume, let the heat supplied to the system is 'q_v' then first law of thermodynamics can be written as

$$\Delta E = q_v + w$$

Since $w = -P\,\Delta V$

$$\Delta E = q_v - P\,\Delta V$$

Since volume is constant, therefore, $\Delta V = 0$

Thus $\Delta E = q_v$

- *It means that heat exchanged at constant volume is used to change the internal energy of the system and no work is done.*

HEAT CHANGES AT CONSTANT PRESSURE (ENTHALPY)

Enthalpy

Enthalpy of a system is the sum of its internal energy and product of pressure and volume (PV). It represents the total heat content of a system."

Mathematically

$$H = E + PV$$

Explanation

At constant pressure, when heat is supplied to the system, a part of this heat is used to increase the internal energy of a system and a part is used to do P-V work. Thus enthalpy is used to represent the change in state of the system.

<u>Enthalpy is also called total heat content of the system.</u>

Properties

1. It is a <u>state function</u>
2. Its unit is <u>Joule (J)</u>
3. It <u>cannot</u> be determined for a system in a given state. <u>Only change in enthalpy</u> can be determined.

Since enthalpy is

$$H = E + PV$$

Change in enthalpy is given by

$$\Delta H = \Delta E + \Delta (PV)$$

$$\Delta H = \Delta E + V\Delta P + P\Delta V$$

At constant pressure, $\Delta P = 0$

$$\Delta H = \Delta E + P\Delta V \quad \text{\_\_ (1)}$$

According to first law of thermodynamics at constant P

$$\Delta E = q_p + w$$

Since $w = -P\Delta V$

$$\Delta E = q_p - P\Delta V \quad \text{\_\_\_ (2)}$$

Put eq (2) in eq (1)

$$\Delta H = q_p - P\Delta V + P\Delta V$$

$$\Delta H = q_p$$

- *It means that heat exchanged at constant pressure is used to change the enthalpy of a system*
- *Most of the chemical reactions are carried out at constant pressure, therefore, ΔH is more important than ΔE for a chemist.*

Difference between internal energy and enthalpy

	Internal energy		Enthalpy
1	It is the total energy of the system.	1	It is sum of the Internal energy and the product of pressure and volume (PV) of the system.
2	It is the sum of all types of kinetic and potential energies of a system.	2	It is sum of the internal energy and the product of pressure and volume (PV) of the system.
3	Mathematically, it is given as $E = K.E. + P.E.$	3	Mathematically, it is given as $H = E + PV$
4	It is denoted by 'E'.	4	It is denoted by 'H'.

Exercise Q 7 (b)

How will you differentiate between ΔE and ΔH? Is it true that ΔH and ΔE have the same values for the reactions taking place in the solution state.

ΔH is the heat change at constant pressure (Enthalpy Change) and

ΔE is the heat change at constant volume (Internal Energy Change)

Difference between internal energy change and enthalpy change

	Internal Energy Change (ΔE)		Enthalpy Change (ΔH)
1	The amount of heat evolved or absorbed at constant volume is called internal energy change ($q_v = \Delta E$)	1	The amount of heat evolved or absorbed a constant pressure is called enthalpy change. ($q_p = \Delta H$)
2	Mathematically, $\Delta E = q + w$ or $\Delta E = \Delta H - P\Delta V$	2	Mathematically, $\Delta H = \Delta E + P\Delta V$
3	It is denoted by ΔE.	3	It is denoted by ΔH.

Relationship Between ΔH & ΔE for Solution

Change in Enthalpy is given by

$$\Delta H = \Delta E + P\Delta V$$

For reactions involving only solids and liquids, or in solution state the change in volume is zero. i.e. $\Delta V = 0$

Hence $\Delta H \cong \Delta E$

Thus ΔH and ΔE have same values for reactions taking place in solution state.

Example I

When 2 moles of H_2 and 1 mole of O_2 at 100°C and 1 torr pressure react to produce 2 moles of gaseous water, 484.5 kJ of energy are evolved.

(Sargodha Board, 2012; Multan Board, 2012; Bahawalpur Board, 2012)

Solution:

What are (a) ΔH (b) ΔE for the production of one mole of H_2O

The reaction is

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$$

Since heat evolved is for two moles of $H_2O_{(g)}$, therefore, heat evolved for one mole at constant P will be

$$q_p = \Delta H = \frac{-484.5}{2} = \boxed{-242.25 \text{ kJ/mol}} \quad \_\_\_ (1)$$

Δn = No. of moles of product – No. of moles of reactants

$\Delta n = 2 - 3 = -1$

$T = 100°C + 273 = 373$ K

$P = 1$ atm

$R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}$

Since $\Delta H = \Delta E + P\Delta V$

$\Delta E = \Delta H - P\Delta V$ ___ (2)

Let $PV = nRT$

and $\Delta(PV) = \Delta nRT$

or $V\Delta P + P\Delta V = \Delta nRT$

Since P = constant, therefore $\Delta P = 0$

$P\Delta V = \Delta nRT$

$= -1 \times 8.314 \times 373$

$= -3100$ J

or $P\Delta V = -3.1$ kJ

This amount is for 2 moles of $H_2O_{(g)}$, therefore, for one mole we have

$$P\Delta V = \frac{-3.1}{2} = -1.55 \text{ kJ/mol} \quad \_\_\_ (3)$$

Put value of ΔH from eq (1) and value of $P\Delta V$ from eq (3) in eq (2), we get

$\Delta E = \Delta H - P\Delta V$

$\Delta E = -242.25 - (-1.55) = \boxed{-240.7 \text{ kJ/mol}}$

Standard State

The natural physical state of a substance at 25°C (298K) and 1 atm pressure is known as standard state of the substance e.g;

- The standard state of CO_2 is gas
- The standard state of H_2O is liquid.
- The standard state of Fe is solid.

Exercise Q5 (b) *Define the following enthalpies and give two examples of each.*

(i) Standard enthalpy of reaction
(ii) Standard enthalpy of combustion
(iii) Standard enthalpy of atomization
(iv) Standard enthalpy of solution

Enthalpy of Reaction (ΔH_r°)

The standard enthalpy change which occurs when the number of moles of reactants as indicated by the balanced chemical equation react together completely to give products under standard conditions.

All the reactants and products are in their standard physical states.

- In exothermic reactions, enthalpy of product is less than enthalpy of reactant. Hence heat is evolved and ΔH_r° is negative. e.g.:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.7 \text{ kJ/mol}$$
$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)} \quad \Delta H = -285.8 \text{ kJ/mol}$$

- In endothermic reactions, enthalpy of product is greater than enthalpy of reactants. Hence, heat is absorbed and ΔH_r° is positive.

$$N_{2(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$$
$$\Delta H = +180.51 \text{ kJ/mol}$$

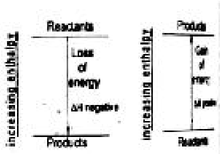


Figure: Enthalpy changes of thermochemical reactions

Enthalpy of formation (ΔH_f°)

The change of enthalpy when 1 mole of the compound is formed from its element, in their standard state is known as standard enthalpy of formation of the compound.

Examples:

$$Mg_{(s)} + \tfrac{1}{2} O_{2(g)} \longrightarrow MgO_{(s)} \quad \Delta H_f^\circ = -692 \text{ kJ/mol.}$$
$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H_f^\circ = -393.7 \text{ kJ/mol}$$

Enthalpy of Atomization (ΔH_{at}°)

The enthalpy change when one mole of gaseous atoms are formed from the element under standard conditions is called standard enthalpy of atomization of an element.

Example:

$$\tfrac{1}{2} H_{2(g)} \longrightarrow H_{(g)} \quad \Delta H_{at}^\circ = 218 \text{ kJ/mol}$$

Enthalpies of atomization can be determined by various methods.

Exercise Q9.
Define heat of neutralization. When a dilute solution of a strong acid is neutralized by a dilute solution of a strong base, the heat of neutralization is found to be nearly the same in all the cases. How do you account for this?

Enthalpy of Neutralization (ΔH_n°)

The amount of heat evolved when one mole of hydrogen ions (H^+), from an acid, react completely with one mole of hydroxide ions (OH^-), from a base to form one mole of water is called enthalpy of neutralization.

Example:

The enthalpy of neutralization of NaOH with HCl is –57.4 kJ/mol

$$NaOH + HCl \rightarrow NaCl + H_2O \quad \Delta H_n^\circ = -57.4 \text{ kJ/mol}$$

- ***Enthalpy of neutralization of a strong acid with strong base is always approximately constant i.e. – 57.4 kJ/mol***

Example:

HCl is a strong acid and NaOH is a strong base

Both ionizes in water completely

$$HCl_{(aq)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$
$$NaOH_{(aq)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$$

On mixing these solutions, H^+ and OH^- ions react together to form water and heat is evolved. While Na^+ and Cl^- ions are set free in such solution.

Thus, heat released during this process is actually the heat of formation of liquid H_2O from H^+ and OH^- ions.

$$Na^+_{(aq)} + OH^-_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \longrightarrow H_2O + Na^+_{(aq)} + Cl^-_{(aq)}$$

Or

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)} \quad \Delta H_n^\circ = -57.4 \text{ kJ/mol}$$

Equivalent amounts of all strong acids produce same amount of H^+ ions in solution. Also equivalent amounts of all strong bases produce same amount of OH^{-1} ions in solution.

Since, the net reaction is between H^+ and OH^{-1} ions, so, the heat of neutralization by strong acid with strong base is always constant (– 57.4 kJ/mol).

Enthalpy of combustion (ΔH_c°)

The enthalpy change when one mole of a substance is completely burnt in excess of oxygen under standard conditions is called standard enthalpy of combustion of a substance.

Example

$$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)} \quad \Delta H_c^\circ = -1368 \text{ kJ/mol}$$

Enthalpy of solution (ΔH°_{sol})

The amount of heat absorbed or evolved when one mole of a substance is dissolved in so much solvent that further dilution results in no detectable heat change is called enthalpy of solution of substance.

Examples

1. Enthalpy of solution of NH_4Cl is $+16.2$ kJ/mol.
   During this heat is absorbed from surrounding and solvent is cooled. It is an endothermic process.
2. Enthalpy of solution of Na_2CO_3 is -25 kJ/mol.
   During this heat is released and temperature of the solvent rises. It is an exothermic process.

MEASUREMENT OF ENTHALPIES

Exothermic and endothermic reactions can be identified by noting the temperature change.

For accurate measurement of ΔH, calorimeters are used.

Two types of calorimeters are generally used

1. Glass calorimeter
2. Bomb calorimeter

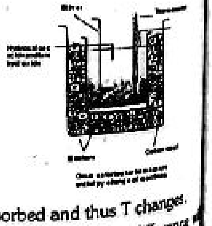
> **Specific Heat**
> ***The amount of heat required to increase the T of one gram of a substance by one Kelvin.***
> It is expressed in $J\ g^{-1}$

How ΔH can be determined by using glass Calorimeter? *(Faisalabad Board, 2009)*

1. GLASS CALORIMETER

Construction

It consists of an ordinary glass, which is insulated from the surroundings by cotton wool as shown in the fig. It is provided with a stirrer and a thermometer for noting T change.



Stoichiometric amounts of substances are placed in calorimeter. When reaction starts, heat is either evolved or absorbed and thus T changes.

The T of the system is noted before and after the chemical reaction. The difference will give the T change (ΔT)

Figure: Glass Calorimeter

If mass of reactants is "m" and specific heat of reaction mixture is "s", then amount of heat "q" evolved or absorbed is determined by the eq.

$$q = m \times s \times \Delta T$$

Example 2

Neutralization of 100 cm³ of 0.5M NaOH at 25°C with 100 cm³ of 0.5M HCl at 25°C, raised the temperature of reaction mixture to 28.5°C. Find the enthalpy of neutralization. Specific heat of water= 4.2 J g⁻¹ K⁻¹ *(Gujranwala Board, 2012. Multan Board, 2012)*

Solution:

→ Volume of acid/ or base used $= V = 100\ cm^3$
Initial temperature $= T_1 = 25\ °C$
Final temperature $= T_2 = 28.5\ °C$
Rise in temperature $= \Delta T = 28.5 - 25 = 3.5\ °C = 3\ K$
Specific heat of water $= s = 4.2\ J\ g^{-1}\ K^{-1}$

→ Since density of solution (water) $= d = 1\ g\ cm^{-3}$
Total volume of solution $= V = 100\ cm^3 + 100\ cm^3 = 200\ cm^3$
So, mass of solution $= m = d \times V$
$= 1 \times 200 = 200\ g$.

→ Thus, heat evolved is given by
$q = m \times s \times \Delta T$
$= 200 \times 4.2 \times 3.5 = 2940\ J = 2.94\ kJ$
or $q = -2.94\ kJ$ (exothermic reaction)

→ Since Molarity of acid/ or base used $= M = 0.5\ M$, therefore
$1000\ cm^3$ of solution contain HCl $= 0.5$ moles
$100\ cm^3$ of solution contain HCl $= \frac{0.5}{1000} \times 100 = 0.05$ moles

→ Hence
0.05 moles of HCl react with 0.05 moles of NaOH
Thus heat of neutralization is given by
0.05 moles of HCl produce heat $= -2.94\ kJ$
1 mole of HCl produce heat $= -\frac{2.94}{0.05} = -58.5$ kJ/mol

Hence heat of neutralization $= \Delta H^{\circ}_{n} = \boxed{-58.8\ kJ/mol}$

Exercise Q8 (b)

How do you measure the heat of combustion of a substance by bomb calorimeter?

2. BOMB CALORIMETER

It is used for accurate determination of heat of combustion of food, fuel and other substances.

Construction

- It consists of a <u>cylindrical steel vessel (steel bomb)</u>, lined with <u>enamel</u> to prevent <u>corrosion</u> and a screw valve at the top.
- A <u>platinum crucible</u> is present inside steel bomb.
- There is also present an <u>electrical ignition coil</u>.
- The bomb is <u>immersed</u> in a <u>known mass</u> of H_2O in an <u>insulated calorimeter</u> as shown in fig. The temperature is measured with a thermometer.

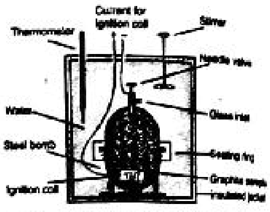


Figure: Bomb Calorimeter

Working

- A <u>known mass (about one gram)</u> of the test <u>substance</u> is placed on a platinum crucible. The lid is closed and oxygen is supplied inside until its pressure is <u>20 atm</u>. The calorimeter is <u>immersed in known mass of water</u>. The <u>initial temperature</u> of water is noted. The substance is then <u>ignited</u> electrically by ignition coil.
- The water is stirred and its temperature is noted continuously after every <u>30 sec</u>. The maximum temperature is noted from thermometer.
- The difference of initial and final temperature gives the change in temperature (i.e.; ΔT)

Calculations

- If number of moles of a substance burnt is <u>'m'</u> and specific heat of whole system (calorimeter etc) is <u>'s'</u> in kJ $K^{-1}g^{-1}$, then heat evolved or absorbed <u>'q'</u> is determined by the formula.

$$q = m \times s \times \Delta T$$

The heat capacity 'c' of a system is the product of mass and specific heat and is defined as

" The quantity of heat required to change its temperature by 1 K."

Thus $q = c \times \Delta T$

Example 3

10.16 g of graphite is burnt in a bomb calorimeter and the T. rise recorded is 3.87 K. calculate enthalpy of combustion of graphite if the specific heat of the calorimeter (bomb, water etc.) is 86.02 kJ K^{-1}

<u>Solution:</u>

→ Mass of graphite = 10.16 g

Atomic mass of graphite = 12 g

$$\text{Moles of graphite} = m = \frac{10.16}{12} = 0.843 \text{ moles}$$

Heat capacity = c = 86.02 kJ K^{-1}

Rise in temperature = ΔT = 3.87 K

→ Heat evolved during combustion is given by

$$q = c \times \Delta T$$
$$= 86.02 \times 3.87 = 332.89 \text{ kJ}$$

→ Since

0.843 moles of graphite produce heat = 332.89 kJ

$$1 \text{ mole of graphite produce heat} = \frac{332.89}{0.843} = 395 \text{ kJ/mol}$$

→ Since reaction is exothermic, therefore, heat of combustion of graphite will be negative.

i.e., $\Delta H_c^0 = \boxed{-395 \text{ kJ/mol}}$

Exercise Q11.

(a) Define and explain Hess's law of constant heat summation. Explain it with examples and give its application

(b) Hess's law helps us to calculate the heats of those reactions, which cannot be normally carried out in a laboratory. Explain it

HESS'S LAW OF CONSTANT HEAT SUMMATION

G.H. Hess experimentally discovered it in 1840.

It states

"If a chemical reaction takes place by different ways, the net energy change is same, regardless of the route by which the chemical change occurs, provided the initial and final states are the same.

or

"The net amount of heat evolved or absorbed in a process, including a chemical change, is the same whether the process takes place in one step or in several steps.

<u>Explanation</u>

Consider a process occurring as shown in the figure

Mathematically from figure

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_4$$

$$\begin{tikzcd} A \arrow[r, "\Delta H_4"] \arrow[d, "\Delta H_1"'] & B \\ C \arrow[r, "\Delta H_2"'] & D \arrow[u, "\Delta H_3"'] \end{tikzcd}$$

Thus if system returns to its initial state in a cyclic process, we can write

$$\Sigma \Delta H_{(cycle)} = 0$$

<u>Hence net enthalpy change in a closed cycle is always equal to zero, if the initial and final states are same.</u>

<u>Hess's law is simply an application of Law of Conservation of Energy</u>

PROOF:

Sodium carbonate can be prepared in two ways

First way

$2NaOH_{(aq)} + CO_{2(g)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$ $\Delta H_1 = -89.08\ kJ\ mol^{-1}$

Second way

$NaOH + CO_2 \longrightarrow NaHCO_3$ $\Delta H_2 = -48.06\ kJ\ mol^{-1}$

$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$ $\Delta H_3 = -41.02\ kJ\ mol^{-1}$

According to Hess's law

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$
$$-89.08 = -48.06 - 41.02$$
$$-89.08 = -89.08$$

Hence Hess's law is proved

IMPORTANCE AND APPLICATIONS

There are several processes for which ΔH cannot be determined directly. These are

(i) ΔH_f° of Al_2O_3 and B_2O_3 cannot be determined. It is because, a protective layer is present over the surface of element that resist in complete burning.

(ii) The compound CCl_4 cannot be prepared directly from graphite and chlorine. Moreover, CCl_4 is also not easily decomposed into its constituent elements.

(iii) ΔH_f° of CO cannot be measured directly due to production of CO_2 along with it.

For such reaction heat of reaction is determined indirectly by using Hess's law

Example: (Determination of ΔH_f° for $CO_{(g)}$)

ΔH_f° of CO cannot be measured directly due to production of CO_2 along with it. It can be determined in following ways.

Combustion of carbon can occurs in two ways.

First way

When C is burned in excess of O_2, it is directly converted into CO_2.

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H_1 = -393.7\ kJ\ mol^{-1}$

Second way

When C is burned in limited supply of oxygen CO is formed.

This CO on further oxidation gives CO_2

$C_{(s)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{(g)}$ $\Delta H_2 = ?$

$CO_{(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H_3 = -283\ kJ\ mol^{-1}$

According to Hess's law

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$
or
$$\Delta H_2 = \Delta H_1 - \Delta H_3$$
$$\Delta H_2 = -393.7 - (-283)$$
$$\Delta H_2 = -110.7\ kJ\ mol^{-1}$$

Hence heat of formation of $CO_{(g)}$ is $-110.7\ kJ\ mol^{-1}$.

Q12. (a)

What is lattice energy? How does Born-Haber cycle help to calculate the lattice energy of NaCl?

THE BORN-HABER CYCLE

Lattice Energy

"The amount of energy released when gaseous ions of opposite charges, combine to give one mole of a crystalline ionic compound."

Example:

$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$ $\Delta H = -787\ kJ\ mole^{-1}$

Born-Haber Cycle

It is based on the principle that

The sum of energy changes for a closed cyclic process is zero, if the initial and final states are same

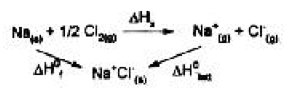
Born-Haber cycle is used to determine lattice energy of ionic crystals. Lattice energy cannot be determined directly. It is determined by a closed Born-Haber cycle.

Example: (Determination of lattice energy of NaCl)

For NaCl, a closed Born-Haber cycle can be drawn as shown in figure. Thus, according to Hess's law,

$$\Delta H_f^\circ = \Delta H_{latt}^\circ + \Delta H_x$$

or, $\Delta H_{latt}^\circ = \Delta H_f^\circ - \Delta H_x$ ____ (1)



Thus if ΔH_f° and ΔH_x are known, then ΔH°_{lat} can be calculated

ΔH_f° of NaCl can be measured in a calorimeter and its value is – 411 kJ mol^{-1}

$$\Delta H_f^\circ = -411 \text{ kJ mol}^{-1} \quad \text{\_\_ (2)}$$

ΔH_x can be calculated as follow

The overall process is

$$Na_{(s)} + \tfrac{1}{2}Cl_2 \longrightarrow Na^+_{(g)} + Cl^-_{(g)} \qquad \Delta H_x = ?$$

This process involves following steps

1. *Atomization of $Na_{(s)}$ to $Na_{(g)}$.*

Energy required for this process is determined from values of its heat of fusion, heat of vaporization and specific heat capacity.

$$Na_{(s)} \longrightarrow Na_{(g)} \qquad \Delta H_{at} = 108 \text{ kJ mol}^{-1}$$

2. *Conversion of $Na_{(g)}$ to $Na^+_{(g)}$ ion.*

This requires ionization energy of $Na_{(g)}$ which can be determined by spectroscopy.

$$Na_{(g)} \longrightarrow Na^+_{(g)} + e^- \qquad \Delta H_i = 496 \text{ kJ mol}^{-1}$$

3. *Atomization of $Cl_{2(g)}$ to $Cl_{(g)}$.*

Energy required for this process is determined by spectroscopy.

$$\tfrac{1}{2}Cl_{2(g)} \longrightarrow Cl_{(g)} \qquad \Delta H_{at} = 121 \text{ kJ mol}^{-1}$$

4. *Conversion of $Cl_{(g)}$ to $Cl^-_{(g)}$.*

This process is the electron affinity of Cl. Its value can also be determined experimently.

$$Cl_{(g)} + e^- \longrightarrow Cl^-_{(g)} \qquad \Delta H_e = -349 \text{ kJ mol}^{-1}$$

Hence

$$\Delta H_x = \Delta H_{at}(Na) + \Delta H_i(Na) + \Delta H_{at}(Cl_2) + \Delta H_e(Na)$$

$$\Delta H_x = 108 + 496 + 121 - 349$$

$$\Delta H_x = 376 \text{ kJ mol}^{-1} \quad \text{\_\_ (3)}$$

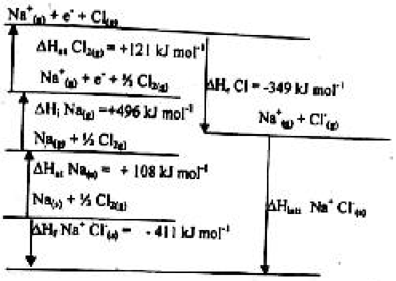
Put values of ΔH_x from eq (3) and ΔH_f° from eq (2) in eq (1), we get

$$\Delta H^\circ_{lat} = \Delta H_f^\circ - \Delta H_x$$

$$\Delta H^\circ_{lat} = -411 - (376) = -787 \text{ kJ mol}^{-1}$$

Hence, lattice energy of NaCl is –787 kJ mol^{-1}. It represents the forces of attraction in NaCl crystals. Lattice energies are used to explain structure, bonding and properties of ionic compounds.

The complete Born-Haber cycle for NaCl is shown in the fig.



OBJECTIVE AND SHORT ANSWER QUESTIONS (EXERCISE)

Q1. Multiple choice questions.

(i) If an endothermic reaction is allowed to take place very rapidly in the air. The temperature of the surrounding air

(a) remains constant (b) increases
(c) decreases (d) remain unchanged

(Gujranwala board, 2012) (D. G. Khan Board, 2012) (Faisalabad Board, 2013)

(ii) In endothermic reactions, the heat content of the (D.G. Khan Board, 2009)

(a) products is more than that of reactants (b) reactants is more than of products
(c) both (a) and (b) (d) reactants and products are equal

(iii) Calorie is equivalent to

(a) 0.4184 J (b) 41.84 J (c) 4.184 J (d) 418.4 J

(Faisalabad Board, 2007) (Rawalpindi board, 2012) (Sargodha Board, 2014) (Gujranwala board, 2014)

(iv) The change in heat energy of a chemical reaction at constant temperature and pressure is called

(a) enthalpy change (c) heat of sublimation
(c) bond energy (d) internal energy change

(Faisalabad Board, 2009) (Rawalpindi Board, 2009, 2012) (Gujranwala board, 2013) (Multan Board, 2013)

(v) Which of the following statements is contrary to the first law of thermodynamics?

(a) Energy can neither be created nor destroyed
(b) One form of energy can be transferred into an equivalent amount of other kinds of energy
(c) In an adiabatic process, the work done is independent of its path
(d) Continuous production of mechanical work without supplying an equivalent amount of heat is possible.

(vi) For a given process, the heat changes at constant pressure (q_p) and at constant volume (q_v) are related to each other as

(a) $q_p = q_v$ (b) $q_p < q_v$ (c) $q_p > q_v$ (d) $q_p = q_v/2$

(Bahawalpur Board, 2009, 2011, 2012) (Sargodha Board, 2011, 2013) (Lahore board, 2013) (Gujranwala board, 2008)

(vii) For the reaction $NaOH + HCl \longrightarrow NaCl + H_2O$ the change in enthalpy is called (Gujranwala board, 2009)

(a) heat of reaction (b) heat of formation
(c) heat of neutralization (d) heat of combustion

(viii) The net heat change in a chemical reaction is same whether it is brought about in two or more different ways in one or several steps. It is known as

(a) Henry's law (b) Joule's principle
(c) Hess's law (d) Law of conservation of energy

(Bahawalpur Board, 2010) (Sargodha Board, 2012) (Rawalpindi board, 2011)

(ix) Enthalpy of neutralisation of all the strong acids and strong bases has the same value because

(a) neutralisation leads to the formation of salt and water.
(b) Strong acids and bases are ionic substances
(c) Acids always give rise to H^+ ions and bases always furnish OH^- ions
(d) The net chemical change involve the combination of H^+ and OH^- ions to form water.

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c) In endothermic reactions, heat is absorbed from the surroundings. Thus temperature of the surrounding decreases.	**(ii) Ans: (a)** In endothermic reactions, heat contents (enthalpy) of products are greater than that of reactants. Thus, reactants have to absorb the extra heat and thus ΔH is positive.
(iii) Ans: (c) 1 calorie = 4.184 J	**(iv) Ans: (a)** Heat exchanged at constant temperature and pressure is called enthalpy change.
(v) Ans: (d) If mechanical work is done without supplying an equivalent amount of heat, then energy (i.e. work) is being created which is against the law of conservation of energy.	**(vi) Ans: (c)** Heat changes at constant volume is given by $q_v = \Delta E$, and Heat changes at constant pressure is given by $q_p = \Delta H = \Delta E + P\Delta V$. Hence, q_p is greater than q_v by an amount equal to $P\Delta V$
(vii) Ans: (c) It is a neutralization reaction of an acid with a base. Hence heat evolved during this reaction is called heat of reaction.	**(viii) Ans: (c)** According to Hess's law: The net amount of heat evolved or observed in a process, including a chemical change, is the same whether the process takes place in one step or in several steps.
(ix) Ans: (d) Both strong acids and bases are completely ionized in water. Thus, acids produce maximum H^+ ions while bases produce maximum OH^- ions in water. During reaction of strong acids and strong bases, actual reaction takes place between H^+ and OH^- ions. Hence, enthalpy of neutralization is same for all strong acids and bases. Its value is -57.4 kJ mol^{-1}	

Q2 Fill in the blanks with suitable words.

(i) The substance undergoing a physical or a chemical change forms a chemical ____.
(ii) The change in internal energy ____ be measured.
(iii) Solid which have more than one crystalline forms possess ____ values of heats of formation.
(iv) A process is called ____ if it takes place on its own without any outside assistance.
(v) A ____ is a macroscopic property of a system which is ____ of the path adopted to bring about that change.

Answers: (i) system (ii) can (iii) different (iv) spontaneous (v) state function, independent

Q.3 Indicate the true or false as the case may be.

(i) It is necessary that a spontaneous reaction should be exothermic.
(ii) Amount of heat absorbed at constant volume is internal energy change.
(iii) The work done by the system is given the positive sign.
(iv) Enthalpy is a state function but internal energy is not.
(v) Total heat content of a system is called enthalpy of the system.

Answers:
(i) False (ii) True (iii) False (iv) False (v) True

Q4. Define the following terms and give three examples of each.

(i)	***System***	*Solved on Page 392*
(ii)	***Surroundings***	*Solved on Page 392*
(iii)	***State function***	*Solved on Page 393*
(iv)	***Units of energy***	*Solved on Page 395*
(v)	***Exothermic reactions***	*Solved on Page 389*
(vi)	***Endothermic reactions***	*Solved on Page 390*
(vii)	***Internal Energy of the system***	*Solved on Page 394*
(viii)	***Enthalpy of the system***	*Solved on Page 397*

Q5. (a) Differentiate between the following

(i)	***Internal energy and Enthalpy***	*Solved on Page 398*
(ii)	***Internal energy change and Enthalpy change***	*Solved on Page 398*
(iii)	***Exothermic and Endothermic reactions***	*Solved on Page 390*

(b) Define the following enthalpies and give two examples of each.

(i) Standard enthalpy of reaction
(ii) Standard enthalpy of combustion
(iii) Standard enthalpy of atomization
(iv) Standard enthalpy of solution

Solved on Page 400

Q6. (a) What are spontaneous and non-spontaneous processes? Give examples.

Solved on Page 391

(b) Explain that burning of a candle is a spontaneous process.
(Lahore Board, 2009; Sargodha Board, 2010, 2011; Gujranwala Board, 2010; D.G. Khan Board, 2012; Azad Kashmir Board, 2012; Rawalpindi Board, 2012; Multan Board, 2012)

Burning of candle is a spontaneous process. It requires a small input of energy to start. This reaction is started by a spark. When candle starts burning the reaction goes to completion by itself. So it is a spontaneous process.

(c) Is it true that a non-spontaneous process happens in the universe?
(Rawalpindi Board, 2010; D.G. Khan Board, 2011; Bahawalpur Board, 2012)

OR Non-spontaneous process never happens in the universe. Justify. *(Gujranwala Board, 2009)*

(i) Non-spontaneous processes generally do not occur in nature by itself. However, these processes can be carried out by continuous supply of energy. e.g., water never flows from lower level to higher level. It is a non-spontaneous process. However, this process can be done by using pump and supplying energy.

(ii) Some processes may occur in nature under specific conditions. e.g. consider the following reaction

$$N_2 + O_2 \rightarrow 2NO$$

Both N_2 and O_2 are present in atmosphere. But they do not react. This reaction takes place, when energy is provided by lightning bolt.

Q7. (a) What is the first law of thermodynamics? How does it explain that

(i) $q_v = \Delta E$ (ii) $q_p = \Delta H$

Solved on Page 396

(b) How will you differentiate between ΔE and ΔH? Is it true that ΔH and ΔE have the same values for the reactions taking place in the solution state.

Solved on Page 398

Q8. (a) What is the difference between heat and temperature? Write a mathematical relationship between these two parameters.

Difference between Heat and Temperature

	Heat		Temperature
1	It is the quantity of energy flows that flows across the boundry of system due to T difference b/w system and surrounding.	1	It is the measure of average K.E. of particles of a substance.
2	It depends upon the amount of substance.	2	It does not depend upon the amount of substance.
3	It is not the property of a given system.	3	It is the property of a given system.
4	Heat flows from hot body to cold body.	4	Temperature difference causes the flow of heat.
5	It is a path function.	5	It is a state function.
6	It is commonly determined by calorimeter.	6	It is determined by thermometer.

Mathematical relationship between heat and temperature is

$$q = m \times s \times \Delta T$$

Where 'q' is the amount of heat evolved from a system, when its temperature is changed by ΔT and 's' is the specific heat of the system.

(b) How do you measure the heat of combustion of a substance by bomb calorimeter?

Solved on Page 403

Q9. Define heat of neutralization. When a dilute solution of a strong acid is neutralized by a dilute solution of a strong base, the heat of neutralization is found to be nearly the same in all the cases. How do you account for this?

Solved on Page 401

Q10. (a) State the laws of thermochemistry and show how are they based on the first law of thermodynamics.

First Law of Thermochemistry:

The heat of formation of a compound is always equal to its heat of decomposition but with opposite sign.

Example:

Heat of formation of CO_2 is

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \quad \Delta H = -393.7 \text{ kJ mol}^{-1}$$

Heat of decomposition CO_2 is

$$CO_{2(g)} \longrightarrow C_{(s)} + O_{2(g)} \quad \Delta H = +393.7 \text{ kJ mol}^{-1}$$

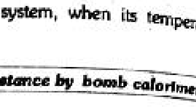
Thus, energy is not created nor destroyed. Hence, it is based upon the first law of thermodynamics

Second Law of Thermochemistry (Hess's Law)

The net amount of heat evolved or absorbed in a process, including a chemical change, is the same whether the process takes place in one step or in several steps.

Mathematically from fig

$$\Delta H_1 + \Delta H_2 + \Delta H_3 = \Delta H_4$$



Thus if system returns to its initial state in a cyclic process, we can write

$$\Sigma \Delta H_{(cycle)} = 0$$

Thus, energy is not created nor destroyed. Hence, it is based upon first law of thermodynamics

(b) What is a thermochemical equation? Give three examples. What information do they convey? *(Multan Board, 2013; Lahore Board, 2012, 2014)*

The thermochemical equations are the chemical equations in which physical states of the reactants/products and amount of heat evolved or absorbed is given.

Example:

$$H_{2(g)} + \tfrac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)} \quad \Delta H = -285.85 \text{ kJ/mol}$$

They tell about the exothermic and endothermic nature of the reactions and quantitative amount of heat evolved or absorbed

(c) Why is it necessary to mention the physical states of reactant and products in a thermochemical equation.

(Multan Board, 2007; Bahawalpur Board, 2008, 2009; Sargodha Board, 2009; D.G Khan Board, 2010; Faisalabad Board, 2012, 2013; Rawalpindi Board, 2013)

Substances have different energies in different physical states. Therefore, heat changes will be different in different reaction, when same substance is involved in different physical states.

e.g. heat of formation of liquid water and heat of formation of water in vapour phases are different i.e.

$$H_{2(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow H_2O_{(g)} \quad \Delta H = -241 \text{ kJ/mol}$$

$$H_{2(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H = -285.85 \text{ kJ/mol}$$

Hence, it is necessary to mention physical states of substances in thermochemical equations.

Q11. (a) Define and explain Hess's law of constant heat summation. Explain it with examples and give its application

Solved on Page 405

(b) Hess's law helps us to calculate the heats of those reactions, which cannot be normally carried out in a laboratory. Explain it

Solved on Page 405

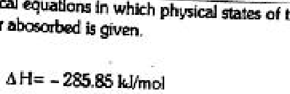
Q12. (a) What is lattice energy? How does Born-Haber cycle help to calculate the lattice energy of NaCl?

Solved on Page 407

(b) Justify the heat of formation of compound is the sum of all the other enthalpies

For NaCl, a closed Born-Haber cycle can be drawn as shown in figure. Thus, according to Hess's law,

$$\Delta H_f^\circ = \Delta H_{latt}^\circ + \Delta H_x$$



Where, ΔH_f° = Enthalpy of formation

ΔH_{latt}° = Lattice energy

ΔH_x = Enthalpy of conversion of Na and Cl into Na^+ and Cl^- ions.

Hence, this equation shows that heat of formation (ΔH_f°), is the sum of all other enthalpies.

NUMERICAL PROBLEMS (Exercise)

Q13. *50 cm³ of 1.0 M HCl is mixed with 50 cm³ of 1.0 M NaOH in a glass calorimeter. The temperature of the resultant mixture increases from 21.0°C to 27.5°C. Assume that calorimeter losses of heat are negligible. Calculate the enthalpy change mole⁻¹ for the reactions. The density of solution to be considered is 1 g cm⁻³ and specific heat is 4.18 J g⁻¹ K⁻¹.*

Volume of acid/ or base used $= V = 50\ cm^3$
Initial temperature $= T_1 = 21\ ^\circ C$
Final temperature $= T_2 = 27.5\ ^\circ C$
Rise in temperature $= \Delta T = 27.5 - 21 = 6.5\ ^\circ C$
Specific heat of water $= s = 4.18\ J\,g^{-1}\,K^{-1}$

Since density of solution (water) $= d = 1\ g\,cm^{-3}$
Total volume of solution $= V = 50\ cm^3 + 50\ cm^3 = 100\ cm^3$
So, mass of solution $= m = d \times V = 1 \times 100 = 100\ g$.

Thus, heat evolved is given by

$q = m \times s \times \Delta T$
$= 100 \times 4.18 \times 6.5 = 2717\ J = 2.717\ kJ$
or $q = -2.717\ kJ$ (exothermic reaction)

Since Molarity of acid/ or base used = M = 1.0 M, therefore
1000 cm³ of solution contain HCl = 1.0 moles

50 cm³ of solution contain HCl $= \frac{1.0}{1000} \times 50 = 0.05$ moles

Hence
0.05 moles of HCl react with 0.05 moles of NaOH
Thus heat of neutralization is given by
0.05 moles of HCl produce heat $= -2.717\ kJ$

1 mole of HCl produce heat $= -\frac{2.717}{0.05} = -54.34\ kJ/mol$

Hence heat of neutralization $= \Delta H_n^o = \boxed{-54.34\ kJ/mol}$

Q14. *Hydrazine (N_2H_4) is a rocket fuel. It burns in O_2 to give N_2 and H_2O*

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

1.0 g. of N_2H_4 is burned in a bomb calorimeter. An increase of temperature 3.51°C is recorded. The heat capacity of calorimeter is 5.5 kJ K⁻¹. Calculate the quantity of heat evolved. Also calculate the heat of combustion of 1 mole of N_2H_4.

Solution:

Mass of hydrazine $= m = 1\ g$

Heat capacity $= c = 5.5\ kJ\,K^{-1}$
Rise in temperature $= \Delta T = 3.51\ ^\circ C$

Heat evolved during combustion is given by

$q = c \times \Delta T$
$= 5.5 \times 3.51 = 19.305\ kJ$

Since reaction is exothermic, therefore
$q = -19.305\ kJ$

Molecular mass of hydrazine (N_2H_4) = 32 g mol⁻¹ = 1 mol
Since
1 g of hydrazine produce heat $= -19.305\ kJ$
32 g of hydrazine produce heat $= -19.305 \times 32 = -617.76\ kJ/mol$
Hence heat of combustion of hydrazine $= \Delta H_c^o = \boxed{-617.76\ kJ/mol}$

Q15. *Octane (C_8H_{18}) is a motor fuel. 1.80 g of a sample of octane is burned in a bomb calorimeter having heat capacity 11.66 kJ K⁻¹. The temperature of the calorimeter increases from 21.36°C to 28.78°C. Calculate the heat of combustion for 1 g of octane. Also, calculate the heat for 1 mole of octane.*

Mass of octane $= m = 1.80\ g$
Heat capacity $= c = 11.66\ kJ\,K^{-1}$
Initial temperature $= T_1 = 21.36\ ^\circ C$
Final temperature $= T_2 = 28.78\ ^\circ C$
Rise in temperature $= \Delta T = 28.78 - 21.36 = 7.42\ ^\circ C$

Heat evolved during combustion is given by

$q = c \times \Delta T$
$= 11.66 \times 7.42 = 86.52\ kJ$

Since reaction is exothermic, therefore
$q = -86.52\ kJ$

Molecular mass of octane = 114 g mol⁻¹ = 1 mole
Since
1.80 g of octane produce heat $= -86.52\ kJ$

1 g of octane produce heat $= -\frac{86.52}{1.8} \times 1 = -48.067\ kJ$

114 g of octane produce heat $= -\frac{86.52}{1.8} \times 114 = -5479.6\ kJ/mol$

Hence heat of combustion of octane $= \Delta H_c^o = \boxed{-5479.6\ kJ/mol}$

Q16. By applying Hess's law calculate the enthalpy change for the formation of an aq. solution of NH_4Cl from NH_3 gas and HCl.

Solution:

Given

$NH_{3(g)} + aq \longrightarrow NH_{3(aq)}$ $\Delta H = -35.16\ kJ\ mol^{-1}$ ___ (1)

$HCl_{(g)} + aq \longrightarrow HCl_{(aq)}$ $\Delta H = -72.41\ kJ\ mol^{-1}$ ___ (2)

$NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$ $\Delta H = -51.48\ kJ\ mol^{-1}$ ___ (3)

Required

$NH_{3(g)} + HCl_{(g)} + aq \longrightarrow NH_4Cl_{(aq)}$ $\Delta H = ?$

Adding eq (1), (2) and (3)

$NH_{3(g)} + aq \longrightarrow NH_{3(aq)}$ $\Delta H = -35.16\ kJ\ mol^{-1}$

$HCl_{(g)} + aq \longrightarrow HCl_{(aq)}$ $\Delta H = -72.41\ kJ\ mol^{-1}$

$NH_{3(aq)} + HCl_{(aq)} \longrightarrow NH_4Cl_{(aq)}$ $\Delta H = -51.48\ kJ\ mol^{-1}$

$NH_{3(g)} + HCl_{(g)} + aq \longrightarrow NH_4Cl_{(aq)}$ $\Delta H = \boxed{-159.05\ kJ\ mol^{-1}}$

Hence heat of formation of aq solution of NH_4Cl is $-159.05\ kJ\ mol^{-1}$

Q17. Calculate the heat of formation of ethyl alcohol from the following information
Heat of combustion of ethyl alcohol is -1367 kJ/mol
Heat of formation of CO_2 is -393.7 kJ/mol
Heat of formation of H_2O is -285.8 kJ/mol

Given

Heat of combustion of liquid ethanol $C_2H_5OH_{(l)}$

$C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H = -1367\ kJ/mol$ ___ (1)

Heat of formation of $CO_{2(g)}$

$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.7\ kJ/mol$ ___ (2)

Heat of formation of liquid $H_2O_{(l)}$

$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(l)}$ $\Delta H = -285.8\ kJ/mol$ ___ (3)

Required

Heat of formation of $C_2H_5OH_{(l)}$

$2C_{(s)} + 3H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow C_2H_5OH_{(l)}$ $\Delta H = ?$

Multiplying eq(2) by 2

Multiplying eq(3) by 3

Reversing eq(1), and then adding all the equations, we get

$2C_{(s)} + 2O_{2(g)} \longrightarrow 2CO_{2(g)}$ $\Delta H = -787.4\ kJ$

$3H_{2(g)} + 3/2\ O_{2(g)} \longrightarrow 3H_2O_{(l)}$ $\Delta H = -857.4\ kJ$

$2CO_{2(g)} + 3H_2O_{(l)} \longrightarrow C_2H_5OH_{(l)} + 3O_{2(g)}$ $\Delta H = +1367\ kJ$

$2C_{(s)} + 3H_{2(g)} + 1/2 O_{2(g)} \longrightarrow C_2H_5OH_{(l)}$ $\Delta H = \boxed{-277.8\ kJ/mol}$

Q18. If the heats of combustion of C_2H_2, H_2 and C_2H_6 are -337.2, -68.3 and -372.8 kcalories respectively, then calculate the heat of the following reaction.

$C_2H_2 + 2H_2 \longrightarrow C_2H_6$

Given

Heat of combustion of C_2H_2 is

$C_2H_{2(g)} + 5/2 O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(g)}$ $\Delta H = -337.2\ kcal\ mol^{-1}$ ___ (1)

Heat of combustion of H_2 is

$H_{2(g)} + \frac{1}{2} O_{2(g)} \longrightarrow H_2O_{(g)}$ $\Delta H = -68.3\ kcal\ mol^{-1}$ ___ (2)

Heat of combustion of C_2H_6 is

$C_2H_{6(g)} + 7/2 O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(g)}$ $\Delta H = -372.8\ kcal\ mol^{-1}$ ___ (3)

Required

$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$ $\Delta H = ?$

Multiply eq.(2) by 2

Reverse eq(3)

And writing eq. (1) as such, and then adding all these equations, we get

$C_2H_{2(g)} + 5/2\ O_{2(g)} \longrightarrow 2CO_{2(g)} + H_2O_{(g)}$ $\Delta H = -337.2\ kcal$

$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$ $\Delta H = -136.6\ kcal$

$2CO_{2(g)} + 3H_2O_{(g)} \longrightarrow C_2H_{6(g)} + 7/2\ O_{2(g)}$ $\Delta H = +372.8\ kcal$

$C_2H_{2(g)} + 2H_{2(g)} \longrightarrow C_2H_{6(g)}$ $\Delta H = \boxed{-101\ kcal\ mol^{-1}}$

Q19. Graphite and diamond are two forms of carbon. The enthalpy of combustion of graphite at 25°C is -393.51 kJ/mol and that of diamond is -395.4 kJ/mol. What is the enthalpy of the process? Graphite $\rightarrow$ Diamond at the same temperature.

Solution

Given

$C_G + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.5\ kJ\ mol^{-1}$ ___ (1)

$C_D + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -395.41\ kJ mol^{-1}$ ___ (2)

Required

$C_G \longrightarrow C_D$ $\Delta H = ?$

Reverse eq(2)

And writing eq. (1) as such, and then adding all these equations, we get

$C_G + O_{2(g)} \longrightarrow CO_{2(g)}$ $\Delta H = -393.5\ kJ$

$CO_{2(g)} \longrightarrow C_D + O_{2(g)}$ $\Delta H = +395.41\ kJ$

$C_G \longrightarrow C_D$ $\Delta H = \boxed{+1.91\ kJ\ mol^{-1}}$

Q20. What is meaning of the term enthalpy of ionization? If the heat of neutralization of HCl and NaOH is –57.3 kJ/mol and heat of neutralization of CH_3COOH with NaOH is –55.2 kJ/mol. Calculate the enthalpy of ionization of CH_3COOH.

Enthalpy of Ionization

It is the enthalpy change when 1 mole of substance ionizes in solution to form ions under standard conditions.

Example:

$$CH_3COOH_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H^+_{(aq)} \qquad \Delta H = +2.1\ kJ\ mol^{-1}$$

Solution of Numerical Part:

Given

Heat of neutralization of acetic acid and NaOH is

$$CH_3COOH_{(aq)} + Na^+_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + Na^+_{(aq)} + H_2O$$

or

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H_2O \quad \Delta H = -55.2\ kJ\ mol^{-1} \quad (1)$$

Heat of neutralization of NaOH and HCl is

$$Na^+_{(aq)} + OH^-_{(aq)} + H^+_{(aq)} + Cl^-_{(aq)} \longrightarrow H_2O + Na^+_{(aq)} + Cl^-_{(aq)}$$

or

$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(aq)} \quad \Delta H = -57.3\ kJ\ mol^{-1} \quad (2)$$

Required

Heat of ionazation of acetic acid is given by

$$CH_3COOH_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H^+_{(aq)} \quad \Delta H = ?$$

Reversing eq(2),

Writing eq. (1) as such, and then adding all these equations, we get

$$CH_3COOH_{(aq)} + OH^-_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H_2O \quad \Delta H = -55.2\ kJ$$

$$H_2O_{(aq)} \longrightarrow H^+_{(aq)} + OH^-_{(aq)} \quad \Delta H = +57.3\ kJ$$

$$CH_3COOH_{(aq)} \longrightarrow CH_3COO^-_{(aq)} + H^+_{(aq)} \quad \Delta H = \boxed{+2.1\ kJ\ mol^{-1}}$$

Q21 (a) Define (i) Lattice Energy (ii) Atomization Energy

(b) Draw a complete, fully labelled Born Haber cycle for the determination of KBr.

(c) Using the information given in the table below, calculate the lattice energy of KBr.

$$K_{(s)} + \tfrac{1}{2}Br_{2(l)} \longrightarrow KBr_{(s)} \qquad \Delta H_f = -392\ kJ\ mol^{-1}$$

$$K_{(s)} \longrightarrow K_{(g)} \qquad \Delta H_{at} = +90\ kJ\ mol^{-1}$$

$$K_{(g)} \longrightarrow K^+_{(g)} + e^- \qquad \Delta H_i = +420\ kJ\ mol^{-1}$$

$$\tfrac{1}{2}Br_{2(l)} \longrightarrow Br_{(g)} \qquad \Delta H_{at} = +112\ kJ\ mol^{-1}$$

$$Br_{(g)} + e^- \longrightarrow Br^-_{(g)} \qquad \Delta H_e = -342\ kJ\ mol^{-1}$$

$$K^+_{(g)} + Br^-_{(g)} \longrightarrow KBr_{(s)} \qquad \Delta H_{latt} = ?$$

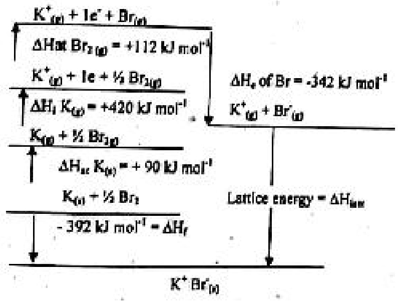
According to Born-Haber cylce

$$\Delta H_{latt} + \Delta H_{at}(K) + \Delta H_i(K) + \Delta H_{at}(Br_2) + \Delta H_e(Br_2) = \Delta H_f$$

or
$$\Delta H_{latt} = \Delta H_f - \Delta H_{at}(K) - \Delta H_i(K) - \Delta H_{at}(Br_2) - \Delta H_e(Br_2)$$

$$= -392 - 90 - 420 - 112 - (-342)$$

$$= \boxed{-672\ kJ\ mol^{-1}}$$



HELLO! Mr. Question here!

Multiple Choice Questions from PAST PAPERS

1. In endothermic reaction ΔH is taken as: (Lahore board, 2014)
   (a) Positive (b) Negative (c) Zero (d) May be any value
2. Whenever a reaction is exothermic, then it means that: (Gujranwala board, 2010)
   (a) the heat is transferred from surroundings to the system
   (b) the heat content of the reactant is greater than products
   (c) the heat content of the reactants is less than those of products
   (d) the heat is transferred from system to the surroundings
3. A state function which describes together the internal energy and the product of pressure and volume is called: (Gujranwala board, 2011)
   (a) enthalpy (b) internal energy (c) work (d) free energy
4. Which of the following is not a state function; (Multan board, 2011)
   (a) Pressure (b) Volume (c) Temperature (d) Heat
5. The Crucible which is used in Bomb Calorimeter is made up of: (Multan board, 2011)
   (a) Glass (b) Copper (c) Gold (d) Platinum
6. For the reaction, $H^+ + OH$, the change in enthalpy is called heat of (Rawalpindi board, 2013)
   (a) reaction (b) combustion (c) solution (d) Neutralization
7. Standard enthalpies are measured at: (Lahore Board, 2009)
   (a) 273k (b) 298k (c) 373k (d) all of these
8. For the reaction $NaOH + HCl \rightarrow NaCl + H_2O$, the change in enthalpy is called: (Sargodha Board, 2009) (D.G. Khan Board, 2011)
   (a) Heat of neutralization (b) Heat of combustion
   (c) Heat of formation (d) Heat of reaction
9. The total heat content of a system is called (Lahore Board, 2010)
   (a) Entropy (b) Enthalpy (c) temperature (d) Internal energy
10. In a bomb calorimeter, the reactions are carried out at constant. (Sargodha Board, 2010)
    (a) pressure (b) temperature (c) volume (d) none of these
11. Formation of NH_3 is an exothermic reaction. However, in Haber's process temperature used is: (Bahawalpur Board, 2010)
    (a) 200°C (b) 300°C (c) 400°C (d) 500°C
12. For the reaction, $NaOH + HCl \longrightarrow NaCl + H_2O$, the change in enthalpy is called (Rawalpindi Board, 2010)

   (a) heat of formation of water (b) heat of formation of NaCl
   (c) heat of neutralization (d) heat of reaction
13. Which one of the following process is an exothermic? (D.G. Khan Board, 2010)
    (a) sublimation (b) respiration (c) Fusion (d) evaporation
14. The exothermic process is (Lahore Board, 2011)
    (a) Evaporation (b) sublimation (c) respiration (d) boiling
15. Standard enthalpy change is measured at
    (a) 298 K (b) 273°C (c) 273 k (d) 373 k
16. The enthalpy change when one mole of a substance is completely burnt in excess of oxygen is called: (Lahore Board, 2007)
    (a) Enthalpy of atomization (b) Enthalpy of neutralization
    (c) Enthalpy of combustion (d) Enthalpy of formation
17. The value of ΔH being very small, the term $\Delta(PV)$ can be neglected, for the process involving: (Faisalabad Board, 2010)
    (a) Liquid and gases (b) liquid and solids
    (c) Solids and gases (d) None of these
18. The enthalpies of all elements in their standard states are: (Multan board, 2010)
    (a) unity (b) zero (c) always positive (d) always negative
19. For the reaction $NaOH + HCl \longrightarrow NaCl + H_2O$ the change in enthalpy is called (D.G. Khan Board, 2012)
    (a) Heat of reaction (b) heat of formation
    (c) heat of neutralization (d) heat of combustion

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(a)	2	(b)	3	(a)	4	(d)	5	(d)
6	(d)	7	(b)	8	(a)	9	(b)	10	(c)
11	(c)	12	(c)	13	(b)	14	(c)	15	(a)
16	(c)	17	(b)	18	(b)	19	(c)		

SHORT & LONG QUESTIONS FROM PAST PAPERS

EXOTHERMIC AND ENDOTHERMIC REACTIONS

Short Questions

(1) *What are exothermic and endothermic reactions. Give one example of each.* **(D.G. Khan Board, 2007: Lahore Board, 2009: Bahawalpur Board, 2010)**
(2) *Why in exothermic reactions, heat is released from the system?* **(Gujranwala Board, 2012)**
(3) *Differentiate between (or Compare) exothermic and endothermic reactions.* **(Faisalabad Board, 2007: Lahore Board, 2011: D.G. Khan Board, 2012: Azad Kashmir Board, 2012: Sargodha Board, 2007, 2012, 2013)**
(4) *What is the cause for the chemical change?* **(Faisalabad Board, 2011)**

SPONTANEOUS AND NON-SPONTANEOUS PROCESS

Short Questions

(1) *What is a spontaneous process? Give examples.* **(Faisalabad Board, 2008: Multan Board, 2009, 2010, 2011: Gujranwala Board, 2014)**
(2) *Give two examples of non-spontaneous reaction?* **(Rawalpindi Board, 2009)**
(3) *What are spontaneous and non-spontaneous processes?* **(Gujranwala Board, 2010)**
(4) *Spontaneous reactions always proceed in the forward direction. Give reason.* OR *Spontaneous are unidirectional. Give reason.* **(Gujranwala Board, 2012)**
(5) *Differentiate between spontaneous and non-spontaneous reactions.* **(Faisalabad Board, 2011: Rawalpindi Board, 2011: D.G. Khan Board, 2012: Multan Board, 2012: Gujranwala Board, 2012: Sargodha Board, 2014)**
(6) *Spontaneous reactions are exothermic in nature. Explain.* **(Gujranwala Board, 2011)**

Long Questions

(1) *Differentiate between (i) Spontaneous and non-spontaneous reaction (ii) Exothermic and Endothermic reaction.* **(Bahawalpur Board, 2009)**
(2) *Differentiate between (i) Internal energy and enthalpy (ii) Exothermic and endothermic reaction.* **(Rawalpindi Board, 2009)**

STATE, STATE FUNCTION, SYSTEM, SURROUNDING, BOUNDARY, INTERNAL ENERGY

Short Questions

(1) *Define state and state functions with examples.* **(Lahore Board, 2008: Gujranwala Board, 2013)**
(2) *What is meant by state function. Explain with two examples.* **(Sargodha Board, 2009: Bahawalpur Board, 2012: Multan Board, 2012: Lahore Board, 2010, 2013, 2014)**
(3) *Define (or describe or differentiate) system and surrounding with one example* **(Gujranwala Board, 2008: D.G. Khan Board, 2009, 2011, 2012: Faisalabad Board, 2010: Bahawalpur Board, 2010: Lahore Board, 2011: Faisalabad Board, 2012: Sargodha Board, 2013)**
(4) *Define system and state function.* **(Sargodha Board, 2011)**
(5) *Temperature is a state function but heat is not. Why?* **(D.G. Khan Board, 2008)**
(6) *What is state function? Prove that internal energy is a state function.*
(7) **(Bahawalpur Board, 2010)**
(8) *Define Internal Energy.* **(Multan Board, 2012)**
(9) *What do you know about internal energy of a system? Give example* **(Bahawalpur Board, 2012: Multan Board, 2012: Lahore Board, 2014)**
(10) *Define the term "Joule" and convert 15 calories to joule* **(Sargodha Board, 2012)**

FIRST LAW OF THERMODYNAMICS, ENTHALPY

Short Questions

(1) *Define first law of thermodynamics. How it is represented mathematically?* **(Lahore Board, 2007: Faisalabad Board, 2009: Multan Board, 2010: Rawalpindi Board, 2011)**
(2) *What is the significance of the equation $\Delta E = q + w$?* **(Rawalpindi Board, 2009)**
(3) *Explain the term enthalpy.* **(Lahore Board, 2013)**
(4) *Prove that change in enthalpy is equal to heat of reaction.* **(D.G. Khan Board, 2010)** OR *Prove that $q_p = \Delta H$* **(D.G. Khan Board, 2012)**
(5) *State why $\Delta H \approx \Delta E$ in case of liquids and solids.* **(Rawalpindi Board, 2007)**
(6) *Differentiate between internal energy and enthalpy* **(Faisalabad Board, 2010, 2011: Rawalpindi Board, 2012)**

Long Questions

(1) *State and explain first law of thermodynamics.* **(Lahore Board, 2009)**
(2) *What is first law of thermodynamics. How does it explain that $\Delta H = q_p$* **(D.G. Khan Board, 2009)**
(3) *Discuss first law of thermodynamics and prove that $\Delta E = q_v$* **(D.G. Khan Board, 2010)** OR *State first law of thermodynamics. Prove that $\Delta E = q_v$* **(Lahore Board, 2013)**
(4) *Explain enthalpy and prove that $\Delta H = q_p$* **(Lahore Board, 2010: Multan Board, 2011)**
(5) *Define system and surrounding. Also prove $\Delta H = q_p$* **(Faisalabad Board, 2010)**
(6) *Prove that $\Delta H = q_p$* **(Lahore Board, 2007: Gujranwala Board, 2010)**
(7) *Prove that change in internal energy of a system at constant volume is equal to heat absorbed by the system.* **(D.G. Khan board, 2007)** OR *Prove that : $\Delta E = q_v$* **(Lahore Board, 2014)**
(8) *Prove that: (i) $\Delta E = q_v$ (ii) $\Delta H = q_p$* **(Gujranwala Board, 2009: D.G. Khan Board, 2011)**

ENTHALPHY OF REACTION, ATOMIZATION, FORMATION, NEUTRALIZATION, COMBUSTION, SOLUTION.

Short Questions

(1) *Define ΔH_f^o. Can it be negative. Why?* **(Multan Board, 2008)**
(2) *What is meant by standard enthalpy of atomization? Give example* **(Faisalabad Board, 2008: Azad Kashmir Board, 2012: Rawalpindi Board, 2012: Lahore Board, 2013: Sargodha Board, 2014)**
(3) *What is meant by standard enthalpy of neutralization? Give an example* **(D.G. Khan Board, 2008: Faisalabad Board, 2009: Rawalpindi Board, 2009: Multan Board, 2012, 2013: Sargodha Board, 2012, 2013: Lahore Board, 2014: Gujranwala Board, 2014)** OR *Enthalpy of neutralization is for an acid and base. Explain with example.* **(Bahawalpur Board, 2011)**
(4) *Comment that enthalpy of neutralization is merely the heat of formation of one mole of liquid water.* **(Lahore Board, 2008)** OR *Enthalpy of neutralization for any strong acid with strong base is same. Explain.* **(Multan Board, 2007: Bahawalpur Board, 2008, 2009)**
(5) *Define/Explain with examples*
 (i) *enthalpy of combustion* **(Multan Board, 2011: D.G. Khan Board, 2009, 2012: Gujranwala Board, 2013)**
 (ii) *enthalpy of atomization and enthalpy of neutralization.* **(Sargodha Board, 2010)**
 (iii) *atomization energy and lattice energy?* **(Rawalpindi Board, 2010)**
 (iv) *standard enthalpy of formation* **(Lahore Board, 2012)**

(v) standard enthalpy of solution (Gujranwala Board, 2008: Sargodha Board, 2013)
(vi) enthalpy of combustion and enthalpy of solution. (Rawalpindi Board, 2013)
(vii) enthalpy of formation and enthalpy of atomization. (Faisalabad Board, 2007)

Long Questions

(1) Define the following. (Rawalpindi board, 2007)
(i) Standard enthalphy of neutralization with example.
(ii) Standard enthalphy of combustion with example.

(2) Define the following:
(i) System (Gujranwala Board, 2011)
(ii Surroundings (Faisalabad Board, 2007: Gujranwala Board, 2011)
(ii) Standard enthalpy of atomization (Faisalabad Board, 2007: Gujranwala Board, 2011)
(iii) Standard enthalpy of solution. (Faisalabad Board, 2007: Gujranwala Board, 2011)

MEASUREMENT OF ENTHALPY OF REACTION

Short Questions

(1) For what purpose bomb calorimeter is used? (Sargodha Board, 2007)

Long Questions

(1) What is enthalpy of a reaction? Name two methods for the determination and explain any one method. (Sargodha Board, 2009)
(2) Define enthalpy of reaction. How the enthalpy of reaction is measured by glass calorimeter? (Sargodha Board, 2013: Lahore Board, 2013)
(3) Define enthalpy of neutralization. Also discuss glass calorimeter in detail? (Gujranwala Board, 2013) OR Staste the construction and working of glass calorimeter. (Gujranwala Board, 2014)
(4) Describe how the enthalpy of combustion (ΔH_c) of a substance is measured by bomb calorimeter? (Faisalabad Board, 2011, 2013: Rawalpindi Board, 2014)

HESS'S LAW OF CONSTANT HEAT SUMMATION, BORN-HABER CYCLE

Short Questions

(1) State the Hess's law of constant heat summation (Lahore Board, 2013: Faisalabad Board, 2013)
(2) Justify that heat of formation of compound is sum of all the other enthalpies. (Lahore Board, 2010)
(3) What is Born-Haber cycle? What is the main advantage of "Born-Haber cycle" (D.G. Khan Board, 2007: Multan Board, 2012)
(4) Draw a fully labelled "Born-Haber cycle" for the formation of NaCl (Multan Board, 2009)

Long Questions

(1) Describe or Define or State "Hess's law of constant heat summation" with an example (Gujranwala Board, 2008: Multan Board, 2010, 2013: Sargodha Board, 2007, 2010, 2011, 2014: Rawalpindi Board 2010: Lahore Board 2011, 2012, 2014: Faisalabad Board 2011)
(2) Define Lattice Energy and Born-Haber cycle. How lattice energy is measured by Born-Haber cycle. Write equation of different enthalpy changes in the formation of NaCl from its elements. (Bahawalpur Board, 2011: Sargodha Board, 2013)

TEST YOUR SKILLS

OBJECTIVE

Time: 20 Minutes Marks: 85

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it. Marks: 17

(i) If the system transfers heat to the surrounding, the reaction is said to be
(a) endothermic (b) exothermic (c) neither (d) either

(ii) When work is limited to pressure-volume type, the work done at constant pressure is called
(a) PV (b) $P\Delta V$ (c) ΔPV (d) none

(iii) When reaction is carried out at constant volume and no work is done, the change in internal energy is equal to
(a) q + w (b) q (c) w (d) none

(iv) In a bomb calorimeter, the reactions are carried out at
(a) constant volume (b) constant pressure (d) constant temperature (d) a, b, c condition

(v) Which of the following is the correct equation?
(a) $\Delta E = q - w$ (b) $\Delta w = \Delta E + \Delta q$ (c) $\Delta E = \Delta w + \Delta q$ (d) none

(vi) Evaporation of water is
(a) an exothermic change (b) a chemical reaction
(c) an endothermic change (d) a process where no heat changes occur

(vii) Hess law states, energy of formation of a compound
(a) depends on path (b) does not depend on path (c) both a and b are correct (d) none of the above

(viii) Hess's law deals with
(a) changes in heat of reaction (b) rate of reaction
(c) equilibrium constant (d) influence of pressure on volume of a gas

(ix) Combustion of methane
(a) is an exothermic reaction (b) is an endothermic reaction (c) requires a catalyst (d) gives H_2

(x) Enthaply change for the reaction: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ is called enthalpy of
(a) Formation (b) Combustion (c) Neutralization (d) Atomization

(xi) Neutralization of a strong acid with a strong base is
(a) non-spontaneous reaction (b) spontaneous reaction (c) chemical equilibrium (d) reversible process

(xii) Heat absorbed by a system at constant pressure is equal to
(a) ΔE (b) ΔH (c) E (d) H

(xiii) The enthalpy change of a reaction is the same whether it takes place in one step or in several steps. This is called as
(a) first law of thermodynamics (b) law of thermochemistry (c) Hess's Law (d) Raoult's Law

(xiv) ΔH^0_c is the standard enthalpy when
(a) 1 mole of a compound formed from its elements (b) 1 mole of an ionic compound formed from its ions
(c) 1 mole of a compound burnt in excess of oxygen completely
(d) 1 mole of acid neutralized by strong base

(xv) Standard enthalpy change for a reaction is measured at
(a) 0°C and 1 atm (b) 100°C and 10 atm (c) 25°C and 1 atm (d) 25°C and 10 atm

(xvi) Kinetic energy of the molecules is due to
(a) translational motion (b) rotational motion (c) vibrational motion (d) all above

(xvii) Standard enthalpy of combustion of H_2 is -285.8 kJ mol^{-1} then which is the standard enthalpy of formation of water
(a) +285.8 kJ mol^{-1} (b) -285.8 kJ mol^{-1} (c) Zero (d) -218 kJ mol^{-1}

SUBJECTIVE

Time: 2:10 Hours Marks: 68

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question numbers carefully. (22x 2)=44

Section - I

Q2. Answer any Eight parts from the followings.
(i) Why it is necessary to mention physical states of substances in a thermochemical equation?
(ii) Differentiate between spontaneous and non-spontaneous process.

(iii) State Hess's law.
(iv) What are state functions? Give examples.
(v) What types of kinetic energies are present in a molecule?.
(vi) Differentiate between heat and temperature.
(vii) Define enthalpy of solution. Give two examples.
(viii) What are the limitations of thermochemistry?
(ix) How will you determine standard heat of CO using Hess's law?
(x) What is the basis of Born-Haber cycle?
(xi) What is pressure volume work ?
(xii) Heat is a path function. Why?

Q3. Answer any Eight parts from the following.

(i) What happens to the temperature of the system during exothermic and endothermic reactions?
(ii) What happens when a piece of zinc is added to the copper sulphate solution?
(iii) How system is separated from surrounding?
(iv) What is internal energy?
(v) How energy can be exchaged between system and surrounding?
(vi) What is pressure-volume work?
(vii) State first Law of thermodynamics?
(viii) What is the significance of the equation $\Delta E = q + w$?
(ix) Differentiate between heat and temperature?
(x) What is enthalpy?
(xi) What is the significance of the relationship. $\Delta H = \Delta E + P\Delta V$?
(xii) Under what conditions ΔH and ΔE are approximately same?

Q4. Answer any Six parts from the following.

(i) What is standard enthalpy of reaction (ΔH°_r)
(ii) Define Enthalpy of atomization and Enthalpy of Neutralization?
(iii) Burning of a candle is a spontanectis process. Justify.?
(iv) Enthalpy of neutralization of a strong base by a strong acid is always 57.4 kJ/mol. Why?
(v) Standard enthalpy of combustion of ethenol is 1368 kJ/mole, Write down the combustion reaction?
(vi) What is the enthalpy of solution?
(vii) How is the enthalpy of combustion of food, fuel and other compounds determined?
(viii) What is the relationship for calculating the amount of heat evolved or absorbed?
(ix) How is the enthalpy for formation of CO determined by Hess's law?

Section - II (Attempt any three questions) (8x 3)=24

Q3. (a) Describe Born-Haber cycle for NaCl. (04)
(b) Prove that $q_p = \Delta H$ (04)

Q4. (a) Define the following with examples. (4 ½)
(i) Enthalpy of solution (ii) Enthalpy of atomization (iii) Enthalpy of neutralization
(b) Describe briefly the construction and working of Bomb calorimeter. (3 ½)

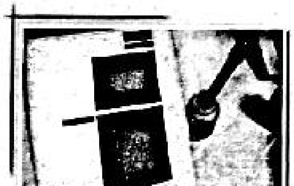
Q5. (a) Define and explain Hess's law with examples. (04)
(b) Give two applications of Hess's law. (03)
(c) Define internal energy. (01)

Q6. (a) Some spontaneous reaction requires energy to start. Explain why? (02)
(b) If the heats of combustion of C_2H_4, H_2 and C_2H_6 are -337.2, -68.3 and -372.8 kcalories respectively then calculate the heat of the following reaction. $C_2H_4 + H_2 \rightarrow C_2H_6$ (03)
(c) What is enthalpy of a reaction? Give one method for its measurement. (03)

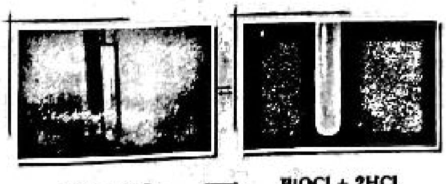
Q7. (a) What are system and surroundings. Explain with examples. (02)
(b) Octane (C_8H_{18}) is a motor fuel. 1.80 g of a sample of octane is burned in a bomb calorimeter having heat capacity 11.66 kJ K^{-1}. The temperature of the calorimeter increases from 21.36°C to 28.78°C. Calculate the heat of combustion for 1 g of octane. Also, calculate the heat for 1 mole of octane (03)
(c) During exothermic reactions, temperature of the system rises and goes above the room temperature. Why? (03)

Chapter 8

CHEMICAL EQUILIBRIUM



Electronic pH meter showing pH = 6.82

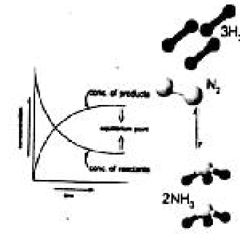


$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$

Adding H_2O Forward Reaction — Adding HCl Backward Reaction

CONTENTS

Chapter-8 **Chemical Equilibrium**



...VERSIBLE AND IRREVERSIBLE REACTIONS

...ercise Q4. (a): *Explain the terms "reversible reaction"*

...ersible Reaction

The reactions, which can proceed both in forward as well as in backward direction, are called ...ersible reactions.

<u>...ample</u>

The reaction of N_2 and H_2 to form NH_3 is a reversible reaction. This reaction occurs at ...°C in the presence of iron as catalyst and under high P.

$$N_2 + 3H_2 \underset{\text{high pressure}}{\overset{Fe/450\,^\circ C}{\rightleftharpoons}} 2NH_3$$

At start, N_2 and H_2 react to form NH_3. However, after sometime NH_3 also decomposes ...ck to N_2 and H_2 because conditions are favourable for both forward as well as for a ...verse reaction. Thus, it is a reversible reaction.

This reaction mixture contain, all the three substances i.e. N_2 , H_2 and NH_3.

<u>...amples:</u>

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$
$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

...reversible Reaction

The reactions, which take place only in one direction, are called irreversible reactions.

Chemical reactions can take place in both directions. However, for some cases, reverse ...action is very small

<u>Example:</u>

Reaction of Na with H_2O produce NaOH and H_2

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

At room temperature, reverse reaction is negligible. It is an irreversible reaction.

Some Reactions are irreversible in under one condition and reversible in other conditions

Example:

- Consider the case of H_2 and O_2 to form H_2O in the presence of electric spark

$$2H_2 + O_2 \longrightarrow 2H_2O$$

- At room temperature, this reaction is negligible in reverse direction. If H_2 and O_2 are mixed in correct proportion then no reactants are left behind.
- However, at 1500°C, H_2O decomposes back to H_2 and O_2. Thus reverse reaction starts.

Hence, at low temperature, this reaction is not reversible. It is called Irreversible reaction.

Difference between Reversible and Irreversible Reactions.

	Reversible reaction		Irreversible reaction
1	The reactions, which can proceed both in forward as well as in backward direction, are called reversible reactions.	1	The reactions, which take place only in one direction, are called irreversible reactions.
2	In these reactions, a dynamic equilibrium is established.	2	In these reactions, equilibrium is not established.
3	Generally, both reactants and products are present at equilibrium state.	3	In these reactions, one or more reactants are almost consumed completely.
4	Examples $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$	4	Examples $2Na + 2H_2O \rightarrow 2NaOH + H_2$

Exercise Q4. (a): *Explain the terms "state of equilibrium"*

STATE OF CHEMICAL EQUILIBRIUM

The state of reversible reaction in which rate of forward reaction becomes equal to rate of reverse reaction is called chemical equilibrium.

Explanation

Consider a general reaction

$$A + B \rightleftharpoons C + D$$

In the beginning A & B reacts to give products & this is the only reaction taking place at faster rate

$$A + B \longrightarrow C + D$$

However as soon as some products are formed, the reverse reaction starts at slower rate

$$A + B \longleftarrow C + D$$

As time passes, forward reaction slows down and reverse reaction speeds up and after some period rates of forward and reverse reaction becomes equal and thus a dynamic equilibrium is established. At this stage, concentrations of reactants and products become constant.

$$A + B \rightleftharpoons C + D$$

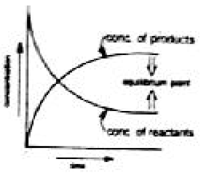


Figure: Reversible reaction and state of equilibrium

It has been shown in the graph. The concentration graph running parallels to the time axis represents the equilibrium state.

Example

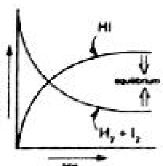
$H_{2(g)}$ and $I_{2(g)}$ reacts at 425°C to form $HI_{(g)}$.

At equilibrium, the concentration of H_2 and I_2 and HI becomes constant. These are not changed with time and a dynamic equilibrium is established.

$$H_{2(g)} + I_{2(g)} \xrightleftharpoons{425°C} 2HI_{(g)}$$

When rising curve of products and falling curve of reactants becomes parallel to time axis, equilibrium is established as shown in the fig.

Further, same concentration is obtained whether the reaction is carried out by reacting $H_{2(g)}$ and $I_{2(g)}$ or by decomposing $HI_{(g)}$.



It shows that there may be two possibilities

- Either all the reactions have stopped in the system and the system becomes stationary.
- Or both forward and reverse reactions are occurring at the same rate.

Second possibility is generally accepted. Hence a chemical equilibrium is called as a dynamic equilibrium.

Exercise Q4 (b):
Define and explain the law of mass action and drive the expression for the equilibrium constant K_c.

LAW OF MASS ACTION

C.M. Guldberg & P Waage gave it in 1864. It states

The rate at which a substance reacts is directly proportional to it active mass, and the rate of a reaction is directly proportional to the product of active masses of the reactants.

Active mass means concentration of reactants and products in mol dm^{-3} in a dilute solution.

Derivation of K_c Expression

Consider a general reaction

$$A + B \rightleftharpoons C + D$$

The active masses of A , B ,C & D in terms of mole dm^{-3} are represented by [A], [B], [C] & [D] respectively.

According to law of mass action

Rate of forward reaction $(R_f) \;\alpha\; [A][B]$

or $R_f = k_f [A][B]$

and Rate of backward reaction$(R_r) \;\alpha\; [C][D]$

or $R_r = k_r [C][D]$

Where k_f = rate constant for forward reaction

k_r = rate constant for backward reaction

At equilibrium state $R_f = R_r$

$$k_f [A][B] = k_r [C][D]$$

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

$$K_c = \frac{[C][D]}{[A][B]}$$

Where K_c= Equilibrium constant

<u>K_c is the ratio of two rate constants.</u>

The subscript 'c' indicates that concentration are expressed in terms of moles /dm^{-3}.

Conventionally, concentrations of products are written above and concentrations of reactants below.

$$K_c = \frac{[Products]}{[Reactants]} \text{ or } K_c = \frac{\text{Rate constants for forward step}}{\text{Rate constants for backward step}}$$

For a reaction

(i) **At a given temperature, value of K_c is independent of the initial concentration of reactants.**

(ii) **The value of K_c varies with temperature**

For a more general reaction

$$aA + bB \rightleftharpoons cC + dD$$

The co-efficients appears as exponents of the concentration terms in the equilibrium constant expression.

i.e., $$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

A state of dynamic equilibrium helps to determine the composition of the reactants and products at the equilibrium.

Units of Equilibrium Constant

Units of K_c depend upon the number of moles of reactants and products involved in the reaction.

1. ***Reaction without change in number of moles***

For such reactions K_c has no unit

e.g. $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \text{No Units}$$

2. ***Reactions with change in number of moles***

For such reactions units of K_c varies from reaction to reaction

e.g. $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[\text{moles dm}^{-3}]^2}{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]^3} = mol^{-2}\, dm^{+6}$$

Example 1

The following reaction was allowed to reach the state of equilibrium.

$$2A + B \rightleftharpoons C$$

The initial amounts of the reactants present in one dm^3 of solution were 0.50 mole of A and 0.60 mole of B. At equilibrium the amounts were 0.20 mole of A and 0.45 mole of B and 0.15 mole of C. Calculate the equilibrium constant K_c

<u>**Solution**</u>

	2A	+ B	⇌ C
Initial conc.	0.50	0.60	0 (mol/dm^3)
Equilibrium conc.	0.20	0.45	0.15 (mol/dm^3)

K_c is given by $$K_c = \frac{[C]}{[A]^2[B]}$$

$$K_c = \frac{[0.15]}{[0.20]^2[0.45]} = \boxed{8.3}$$

Q8. (a): Write down K_c for the following reversible reactions. Suppose that the volume of reaction mixture in all the cases is 'V' dm^3 at equilibrium stage.

EQUILIBRIUM CONSTANT EXPRESSIONS FOR SOME REACTIONS

1. Formation of Ester from an Organic Acid and Alcohol: (Aqueous Phase Reaction)

Alcohol and acid reacts to form ester and water in the presence of small amount of mineral acid as catalyst

$$CH_3COOH + C_2H_5OH \xrightleftharpoons{H_3O^+} CH_3COOC_2H_5 + H_2O$$

The progress of reaction can be noted by finding out the concentrations of acetic acid at regular interval. A small sample of reaction mixture is taken out and amount of acid is determined by titrating it with standard NaOH.

Let initial conc. of acid is 'a' mol/dm³ and that of ethanol is 'b' mol/dm³ and volume of container is 'V' dm³. If at equilibrium, 'x' moles of acetic acid reacts with 'x' moles of ethanol to give 'x' moles of ethyl acetate and 'x' moles of H_2O, then

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial Conc. (moles) (t=0)	a	b	0	0
Equilibrium Conc. (moles) ($t=t_{eq}$)	(a − x)	(b − x)	x	x
Equilibrium Conc. (mol/dm⁻³)	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

According to Law of Mass Action

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{x^2}{(a-x)(b-x)}$$

The final K_c expression contains no V term. Hence volume changes (or pressure changes) does not affect K_c or equilibrium position of reaction.

2. Dissociation of PCl_5 (Gas Phase Reaction)

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

If initial conc. of PCl_5 is 'a' and volume of container is V dm³ and at equilibrium x moles of PCl_5 dissociates to give x moles of PCl_3 and x moles of Cl_2, then

	PCl_5	PCl_3	Cl_2
Initial conc. (In moles) (t=0)	a	0	0
Equilibrium conc. (in moles) ($t=t_{eq}$)	a − x	x	x
Equilibrium conc./V (mol/dm⁻³)	$\frac{(a-x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

According to law of Mass Action

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{(a-x)V}$$

The final K_c expression contains V term. Hence K_c and equilibrium position of reaction is affected by volume and pressure changes.

3. Decomposition of N_2O_4 (Gas Phase Reaction)

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

	N_2O_4	$2NO_2$
Initial conc. (In moles) (t=0)	a	0
Equilibrium conc. (In moles) ($t=t_{eq}$)	a − x	2x
Equilibrium conc./V (mol/dm⁻³)	$\frac{(a-x)}{V}$	$\frac{2x}{V}$

K_c is given by

$$K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)}$$

$$K_c = \frac{4x^2 \cdot V}{(a-x) \cdot V^2} = \frac{4x^2}{(a-x)V}$$

The final K_c expression contains V term. Hence K_c is affected by volume and pressure changes.

4. Synthesis of NH_3 (Gas Phase Reaction)

	$N_{2(g)}$ +	$3H_{2(g)}$ ⇌	$2NH_{3(g)}$
initial conc. (in moles) (t=0)	a	b	0
Equilibrium conc. (in moles) ($t=t_{eq}$)	$a-x$	$b-3x$	$2x$
Equilibrium conc./V (mol / dm^{-3})	$\frac{(a-x)}{V}$	$\frac{(b-3x)}{V}$	$\frac{2x}{V}$

K_c is given by

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-3x}{V}\right)^3}$$

$$K_c = \frac{4x^2}{(a-x)V^2} \times \frac{V^4}{(b-3x)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

Thus, co-efficient of balanced chemical equation determines whether the volume term will appear in numerator or denominator

5. Dissociation of HI (Gas Phase Reaction)

	2HI ⇌	H_2 +	I_2
Initial Conc. (moles) (t=0)	a	0	0
Equilibrium Conc. (moles) ($t=t_{eq}$)	$(a-2x)$	x	x
Equilibrium Conc. (mol/dm^{-3})	$\frac{(a-2x)}{V}$	$\frac{x}{V}$	$\frac{x}{V}$

According to Law of Mass Action

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{\left(\frac{x}{V}\right)\left(\frac{x}{V}\right)}{\left(\frac{a-2x}{V}\right)^2} = \frac{x^2}{(a-2x)^2}$$

The final K_c expression contains no V term. Hence volume changes (or pressure changes) does not affect K_c or equilibrium position of reaction.

6. Formation of HI (Gas Phase Reaction)

	H_2 +	I_2 ⇌	2HI
Initial Conc. (moles) (t=0)	a	b	0
Equilibrium Conc. (moles) ($t=t_{eq}$)	$(a-x)$	$(b-x)$	2x
Equilibrium Conc. (mol/dm^{-3})	$\frac{(a-x)}{V}$	$\frac{(b-x)}{V}$	$\frac{2x}{V}$

According to Law of Mass Action

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

The final K_c expression contains no V term. Hence volume changes (or pressure changes) does not affect K_c or equilibrium position of reaction.

Exercise Q7. *(a) Write down the relationship of different types of equilibrium constants. i.e. K_c and K_p for the following general reactions.*

Relationships Between Equilibrium Constants

For a general reaction

$$aA + bB \rightleftharpoons cC + dD$$

K_c for this reaction can be written as

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\text{or Simply } K_c = \frac{C_C{}^c \times C_D{}^d}{C_A{}^a \times C_B{}^b}$$

where C_C, C_D, C_A and C_B are the molar concentrations of C, D, A and B respectively.

If the reactants and products are ideal gases then molar conc. of each gas is proportional to its partial pressure. When the conc. are expressed in terms of partial pressures, the K_p is given as

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Where $P_C{}^c$, $P_D{}^d$, $P_A{}^a$ and $P_B{}^b$ are the partial pressures of C, D, A and B at equilibrium

Relationship Between K_c And K_p

It is given by

$$K_p = K_c \times (RT)^{\Delta n}$$

Where

R = General Gas constant

T = Absolute Temperature

Δn = change in no. of moles in going from reactants to products.

If the number of moles of reactants and products are equal for a gaseous reaction then values of K_c and K_p are same, since $\Delta n = 0$.

Example 2

N_2 and H_2 combine to give NH_3. Calculate K_p for the synthesis of NH_3. When $K_c = 6 \times 10^{-2}$ at 500°C

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(D.G. Khan Board, 2011: Gujranwala Board, 2010, 2014: Lahore Board, 2013: Multan Board, 2013: Rawalpindi Board, 2014)

Solution

$K_c = 6 \times 10^{-2}$

$T = 500°C + 273 = 773\ K$

$R = 0.0821\ \text{atm dm}^3\ \text{mol}^{-1}K^{-1}$

$K_p = ?$

Change in number of moles $= \Delta n = 2 - 4 = -2$

Since

$$K_p = K_c(RT)^{\Delta n}$$

$$K_p = 6 \times 10^{-2}(0.0821 \times 773)^{-2}$$

$$K_p = \frac{6 \times 10^{-2}}{(0.0821 \times 773)^2}$$

$$K_p = \boxed{1.5 \times 10^{-5}}$$

Here K_p is less than K_c

The reactions, which occur with decrease in number of moles, have smaller K_p than K_c and vice versa.

APPLICATIONS OF EQUILIBRIUM CONSTANT

Value of equilibrium constant is specific and constant at constant temperature. It can be used for following applications

1. Prediction of direction of reaction
2. Extent of chemical reaction
3. Effects of various factors on chemical equilibrium (Le-chatelier's principle)

Exercise Q9:

Explain the following two applications of equilibrium constant. Give examples.

(i) Direction of reaction

1. Prediction of Direction of Reaction

If value of K_c is known for a particular reaction at a given temperature, then $\frac{[\text{product}]}{[\text{reactant}]}$ ratio (before reaction attains equilibrium) can predict the direction of reaction.

There may be three cases

Case – I *If* $\frac{[\text{product}]}{[\text{reactant}]} < K_c$

In this case, more product is needed to regain equilibrium. Hence reaction occurs in forward direction

Case – II *If* $\frac{[\text{product}]}{[\text{reactant}]} > K_c$

In this case, more reactant is needed to regain equilibrium. Hence reaction occurs in backward direction.

Case – III If $\frac{[\text{product}]}{[\text{reactant}]} = K_c$

In this case, reaction is at equilibrium and no more reactant or products are formed.

Example 3

Esterification reaction between ethanol and acetic acid was carried out by mixing definite amounts of ethanol and acetic acid alongwith some mineral acid as a catalyst. Samples were drawn out of the reaction mixture to check the progress of the esterification reaction. In one of the samples drawn after time t, the concentrations of the species were found to be $[CH_3COOH] = 0.025$ mol/dm³, $[C_2H_5OH] = 0.032$ mol/dm³, $[CH_3COOC_2H_5] = 0.05$ mol/dm³ and $[H_2O] = 0.04$ mol/dm³. Find out the direction of the reaction if K_c for the reaction at 25°C is 4. *(Sargodha Board, 2014)*

Solution

The esterification reaction is given as

$$CH_3COOH + C_2H_5OH \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

Since volume is same for all substances, therefore, the K_c for the reaction will be

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

The [product]/[reactant] ratio will be

$$\frac{0.05 \times 0.04}{0.025 \times 0.032} = 2.5$$

Since $\frac{[\text{product}]}{[\text{reactant}]} < K_c$ (i.e. 4), therefore, the reaction will proceed in forward direction.

Exercise Q9:

Explain the following two applications of equilibrium constant. Give examples.

(II) Extent of reaction

2. Extent of Chemical Reaction

Value of K_c can also tell the extent of reaction. i.e. how much reaction have occurred?

There may be three cases

Case – I : Value of K_c Very Large

Very large K_c value shows that reaction is almost complete.

Thus at equilibrium there will be very high conc. of products and very low conc. of reactants

Example

$$2O_3 \rightleftharpoons 3O_2$$

Equilibrium constant for this reation is 10^{55} at 25°C

It shows that at room temperature, O_3 is highly unstable and it almost completely decomposed to O_2.

Case – II : Value of K_c Small

Small K_c value shows that the reaction does not proceed appreciable in forward reaction.

Case – III : Value of K_c Very Small

It shows a very little forward reaction. Thus at equilibrium, there will be high concentration of reactants and very low conc. of products

Example

$$2HF_{(g)} \rightleftharpoons H_{2(g)} + F_{2(g)}$$

Equilibrium constant for this reaction is 10^{-13} at 2000°C.

It shows that at 2000°C, HF is stable and it is only slightly decomposed to give product.

3. Effect of Changing in Conditions in Chemical Equilibrium

Equilibrium constant and position of equilibrium are two different things. K_c is equilibrium constant. It has definite value at a given temperature. However $\frac{[\text{product}]}{[\text{reactant}]}$ ratio is called position of equilibrium. It can be changed by changing conditions. e.g. temperature, pressure and concentration etc.

If K_c is large, the equilibrium lies to the right. If K_c is small, the equilibrium lies to the left.

LE-CHATELIER'S PRINCIPLE

It states

If a stress is applied to a system at equilibrium, the system will act in such a way so as to nullify, as far as possible, the effect of that stress.

A system cannot completely cancel the effect of change. It only minimizes the effect of change. Le-Chatelier's principle tells about the position of equilibrium and composition of physical and chemical equilibriums.

i) Effect of Change in Concentration

Consider the hydrolysis of $BiCl_3$

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

K_c is given by

$$K_c = \frac{[BiOCl][HCl]^2}{[BiCl_3][H_2O]}$$

Solution of $BiCl_3$ is cloudy due to formation of BiOCl. Now if HCl is added to this system, the equilibrium will be disturbed. In order to regain equilibrium, the reaction will move in backward direction and solution becomes clearer.

On the other hand if H_2O is added to the system, it will shift the equilibrium in forward direction and the solution will again becomes cloudy.

Thus following are the effects of changing concentrations

- Adding reactant or removing product favours forward reaction.
- Adding product or removing reactant favours backward reaction.

But value of K_c remains constant. Hence, if one of the product is removed continuously, the yield of reversible reaction is increased.

This concept of changing concentration is applied in common ion effect.

ii) Effect of Change in Pressure or Volume

An increase in pressure on an equilibrium system will move the reaction in a direction of decrease in nnumber o f moles (i.e. decreased volume) and vice versa.

The change in pressure can only effect those reactions which involve volume changes. Gaseous reactions involve volume changes, therefore, they are greatly affected by pressure changes.

Example :

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

In this reaction, number of moles of reactants are decreasing from reactants to products. Thus at equilibrium volume of reaction mixture will be less than the volume of reactants taken. Thus, increasing P will shift the equilibrium in forward direction i.e. towards decrease in volume but value of K_c remains constant.

Quantitative Effect of Volume on Equilibrium Position.

Example: Formation of SO_3

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

The mathematical K_c expression for

$$K_c = \frac{4x^2V}{(a-2x)^2(b-x)}$$

Where V = volume of reaction mixture at equilibrium.

a = Initial concentration of SO_2

b = Initial concentration of O_2

x = Moles of O_2 reacted at equilibrium

It shows that if P is decreased then V is increased, therefore, x must decrease to maintain constant value of K_C. Hence reaction moves in backward direction.

Similarly if V is decreased by increasing P, then K_c is decreased. Thus reaction will move in forward reaction to maintain constant value of K_c.

Other Examples

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

Its mathematical K_c expression is

$$K_C = \frac{x^2}{(a-x)V}$$

$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

Its mathematical K_c expression is

$$K_c = \frac{4x^2}{(a-x)V}$$

Both these reactions have volume in the denominater. It is because no. of moles of product are greater than no. of moles of reactants.

Thus if P is increased then V is decreased, therefore, 'x' must also decrease. Hence, the reaction will proceed in backward direction to maintain constant value of K_c.

Pressure will have no effect on the reactions, in which number of moles of reactants and products are same, e.g.

(i) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$

1 mole 1 mole 2 mole

Similarly, reactions of liquid and solids are also not affected by pressure changes, because they do not involve volume changes.

iii) Effect of Temperature

Considering heat as a component of system, an increase in temperature adds heat to the system while decrease in temperature removes heat from the system. Hence according to Le-Chatlier's principle

- Increase in temperature favours Endothermic reaction, while
- Decrease in temperature favours Exothermic reaction.

Value of K_C changes with change in temperature. It is because equilibrium shifts without addition or removal of reactants or products.

Example 1 : Formation of CO_2 from CO

$$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2(g)} + H_{2(g)} \quad \Delta H = -41.84 \text{ kJ/mol}$$

It is an exothermic reaction, hence decrease in temperature favours forward reaction and vice versa.

By decreasing temperature, heat of the system is lost. Thus more CO and H_2O will react to produce more heat. Hence the reaction will go in forward reaction. If this system is heated, then the reaction will go in backward reaction.

Example 2 : solubility of Salts

Consider the solubility of KI

$$KI_{(s)} \rightleftharpoons KI_{(aq)} \qquad \Delta H = +21.4 \text{ kJ/mol}$$

It is an endothermic reaction. Hence increase in T favours forward reaction.

Hence more and more salt is dissolved by increasing T. While cooling results in backward process. Thus $KI_{(s)}$ crystallizes out.

For some salts, heat of solution is almost zero. For such salts change in T has no effect. e.g. formation of $NaCl_{(aq)}$

If substances have negative heat of solution e.g. LiCl , Li_2CO_3 , then their solubility is decreased by increasing temperature.

(iv) Effect of Catalyst

A catalyst is a substance which changes the rate of a chemical reaction without itself being consumed in the process.

Thus catalyst has no effect on the equilibrium composition of the system. It simply increases the rate of forward and backward reaction. Thus, it only decreases the time to reach the equilibrium state.

A catalysts lower the activation energy of the reaction by giving new path to the reaction.

Applications of Le-Chatelier's principle in industry

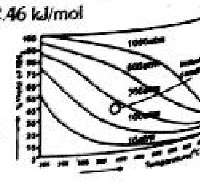
Synthesis of Ammonia by Haber's Process

The process of synthesis of NH_3 was introduced by German chemist F. Haber in 1933.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92.46 \text{ kJ/mol}$$

K_C is given by

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$$



According to Le-Chatelier's principle yield of NH_3 can be increased as follows.

(i) By continuous removal of NH_3 from the reaction mixture, reaction moves in forward direction.

(ii) Since there is decrease in number of moles in going from reactants to products. Hence increase in pressure favours synthesis of NH_3. The pressure used is 200-300 atm.

(iii) Since reaction is exothermic. Hence, decrease in temperature favours forward reaction. The temperature used is 400°C

Hence high pressure, low temperature and continuous removal of NH_3 will give best yield of NH_3.

e.g. Value of K_C at 200 K is 7.17×10^{15} , and at 800 K it is 3.96×10^{-2}.

Decrease in value of K_C shows that increase in T decreases the synthesis of NH_3.

Table Effect of temperature on K_c for ammonia synthesis

T (K)	K_c
200	7.17×10^{15}
300	2.69×10^{8}
400	3.94×10^{4}
500	1.72×10^{2}
600	4.53×10^{0}
700	2.96×10^{-1}
800	3.96×10^{-2}

Optimum Conditions for the synthesis of NH_3

In actual process, following optimum conditions are used

(i) Pressure = 200 – 300 atm
(ii) Temperature = 400°C (673 K)
(iii) Catalyst = Pieces of iron embedded in a fused mixture of MgO, Al_2O_3 and SiO_2
(iv) Continuous removal of ammonia from the reaction mixture.

Removal of NH_3 from the reaction mixture

The equilibrium mixture contain 35% NH_3 by volume. The mixture is cooled by refrigeration coils until NH_3 liquefies at -33.4°C and is removed, while N_2 and H_2 remain in the mixture because they are not liquified at this temperature due to low boiling points. Unreacted N_2 and H_2 are recycled.

- About 13% of nitrogen fixation on earth is carried out by Haber's process.
- Haber's process produce 110 millions tons of NH_3 in the world.
- About 80% of NH_3 is used for making fertilizers. Some NH_3 is used formation explosives, nylons and other polymers.

Synthesis of SO_3

During manufacturing of H_2SO_4, by contact process, SO_2 is oxidised to SO_3.

The reaction is

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \qquad \Delta H = -194 \text{ kJ/mol}$$

According to Le-Chatelier's principle maximum yield of SO_3 can be obtained following ways

(i) Removing SO_3 from reaction mixture or adding more reactants.

(ii) Since there is decrease in number of moles from reactants and products. Hence, increase in pressure favours forward reaction.

(iii) Since reaction is exothermic, hence decrease in temperature favours forward reaction.

Temperature and pressure are the rate controlling factors for this process.

Increasing temperature decreases the yield of SO_3.

e.g. K_c at 200 K is 5500 but at 700 K

It is only 13. Hence formation of SO_3 is less.

High pressure can increase the yield of SO_3. Actually, amount of O_2 is increased to favour forward reaction, instead of increasing pressure.

Table (8.3) Effect of temperature on yield of SO_3

Temp. °C	K_c	Mole % of SO_3
200	5500	98
300	690	91
400	160	75
500	55	61
600	25	46
700	13	31

Optimum Conditions for the synthesis of SO_3

In actual process, following optimum conditions are used

(i) Pressure = 1 atm

(ii) Catalyst = Solid catalyst, V_2O_5 or finally divided Pt

(iii) Temperature = Initial heating of gases at 650°C then recycled at lower temperature of 400-500°C to increase the yield of SO_3

(iv) Continuous addition of O_2

- SO_3 is dissolved in H_2SO_4 to form oleum, which is then diluted with H_2O to get H_2SO_4
- H_2SO_4 is called King of Chemicals. It's use gives an idea of the industrial progress of country.

IONIC PRODUCT OF PURE WATER

Water is a poor conductor of electricity. Because self-ionization of water is very small

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

or

$$H_2O \rightleftharpoons H^+ + OH^-$$

K_c is given by

$$K_c = \frac{[H^+][OH^-]}{[H_2O]} = 1.8 \times 10^{-16}$$

Since 1 dm³ of pure water contains 1000g. Therefore, conc. of H_2O i.e. $[H_2O] = 1000/18 = 55.55$ mol/dm³.

Since H_2O is present in large excess, therefore, its concentration is almost constant.

So, $K_c[H_2O] = [H^+][OH^-]$

or $1.8 \times 10^{-16} \times 55.55 = [H^+][OH^-]$

or $1.01 \times 10^{-14} = K_w = [H^+][OH^-]$

Where $K_c[H_2O] = K_w$ = ionization constant or ionic product of water

Thus, the ionic product of water (K_w) at 25°C is

$$K_w = [H^+][OH^-] = 10^{-14} \qquad \text{\_\_\_ (1)}$$

Effect of temperature on the value of K_w

Value of K_w varies with temperature. It is because, ionization of water increases with increase in temperature. The K_w value increases almost 75 times when temperature is raised from 0°C to 100°C. However, increase in value of K_w is not regular.

This value shows that if 55.5 moles of pure water are present in 1 dm³, then only 10^{-7} moles of water are ionized. It shows that water is very weak electrolyte.

Table (8.4) K_w at various temperature

Temp. °C	K_w
0	0.11×10^{-14}
10	0.30×10^{-14}
25	1.0×10^{-14}
40	3.00×10^{-14}
100	7.5×10^{-14}

Since H_2O gives equal moles of H^+ and OH^- ions.

Hence in neutral H_2O

$$[H^+] = [OH^-]$$

Thus eq (1) can give

$$[H^+][H^+] = 10^{-14}$$

$$[H^+]^2 = 10^{-14}$$

$$[H^+] = 10^{-7} \text{ mole/dm}^3$$

or

$$[OH^-][OH^-] = 10^{-14}$$

$$[OH^-]^2 = 10^{-14}$$

$$[OH^-] = 10^{-7} \text{ mole/dm}^3$$

Thus in neutral water, quantity of $[H^+]$ and $[OH^-]$ ions is always same.

If some acid or base is added to water then K_w remains same but conc. of H^+ and OH^- ions is changed.

If an acid is added then

$$[H^+] > [OH^-]$$

And if a base is added then

$$[OH^-] > [H^+]$$

Exercise Q12. (a) *Define pH and pOH. How are they related with pK_w.*

pH and pOH

pH

In 1909, Sorenson proposed a pH scale, in order to better express the concentration of H^+ ions in aq. solution.

pH is defined as

The negative logarithm of H^+ ions conc. is called pH.

Mathematically $pH = -\log[H^+]$

or ***The logarithm of reciprocal of H^+ ions conc. is called pH.***

Mathematically $pH = \log\dfrac{1}{[H^+]}$

or $pH = \log 1 - \log[H^+]$

$pH = 0 - \log[H^+]$

$pH = -\log[H^+]$

pOH

pOH can be defined as

The negative logarithm of OH^- ions conc. is called pOH.

Mathematically $pOH = -\log[OH^-]$

or ***The logarithm of reciprocal of OH^- ions conc. is called pOH.***

Mathematically $pOH = \log\dfrac{1}{[OH^-]}$

Relationship between pH, pOH and pKw

Since $[H^+][OH^-] = K_w$

Taking log on both sides

$$\log([H^+][OH^-]) = \log K_w$$

$$\log[H^+] + \log[OH^-] = \log K_w$$

Multiply throughout by –ve sign

$$-\log[H^+] - \log[OH^-] = -\log K_w$$

$$(-\log[H^+]) + (-\log[OH^-]) = (-\log K_w)$$

$$pH + pOH = pK_w$$

Since $pK_w = 14$ at 25°C, therefore

$$pH + pOH = 14 \text{ at } 25°C$$

- Negative log of K_w is called pK_w
  - $pK_w = -\log K_w$
  - $pK_w = -\log 10^{-14}$
  - $pK_w = 14 \log 10$
  - $pK_w = 14$ at 25°C
- Value of pK_w is less than 14 at higher temperatures.

Table: Relationship of $[H_3O^+]$, $[OH^-]$, pH and pOH

	$[H_3O^+]$	pH	$[OH^-]$	pOH
Basic	1×10^{-14}	14.0	1×10^{-0}	0.0
	1×10^{-13}	13.0	1×10^{-1}	1.0
	1×10^{-12}	12.0	1×10^{-2}	2.0
	1×10^{-11}	11.0	1×10^{-3}	3.0
	1×10^{-10}	10.0	1×10^{-4}	4.0
	1×10^{-9}	9.0	1×10^{-5}	5.0
	1×10^{-8}	8.0	1×10^{-6}	6.0
Neutral	1×10^{-7}	7.0	1×10^{-7}	7.0
Acidic	1×10^{-6}	6.0	1×10^{-8}	8.0
	1×10^{-5}	5.0	1×10^{-9}	9.0
	1×10^{-4}	4.0	1×10^{-10}	10.0
	1×10^{-3}	3.0	1×10^{-11}	11.0
	1×10^{-2}	2.0	1×10^{-12}	12.0
	1×10^{-1}	1.0	1×10^{-13}	13.0
	1×10^{-0}	0.0	1×10^{-14}	14.0

Exercise Q12 (b):

What happens to the acidic and basic properties of aqueous solutions when pH varies from 0 to 14.

pH Scale

pH scale generally ranges from 0 to 14.

However, solution with negative pH and pH greater than 14 are also known.

Generally, lesser the pH, more acidic is the solution and vice versa.

- pH = 7 solution is neutral
- pH < 7 solutions are acidic
- pH > 7 solutions are basic

Table Approximate pH and pOH of some common materials at 25°C

Material	pH	pOH	Material	pH	pOH
1.0 M HCl	0.1	13.9	Bread	5.5	8.5
0.1 M HCl	1.1	12.9	Potatoes	5.8	8.2
0.1 M CH_3COOH	2.9	11.10	Rain water	6.2	7.8
Gastric juice	2.0	12.00	Milk	6.5	7.5
Lemons	2.3	11.7	Saliva	6.5-6.9	7.5-7.1
Vinegar	2.8	11.2	Pure water	7.0	7.00
Soft drinks	3.0	11.00	Eggs	7.8	6.2
Apples	3.1	10.9	0.1 M $NaHCO_3$	8.4	5.6
Grapefruit	3.1	10.9	Seawater	8.5	5.5
Oranges	3.5	10.5	Milk of magnesia	10.5	3.5
Tomatoes	4.2	9.8	0.1 M NH_3	11.1	2.9
Cherries	3.6	10.4	0.05 M Na_2CO_3	11.6	2.4
Bananas	4.6	9.4	0.1 M NaOH	13.0	1.00

IONIZATION CONSTANT OF ACIDS (Ka)

Acids ionize in water either partially or completely. Many acids are weak electrolytes and they are not 100% ionized.

The strength of acids can be expressed in terms of K_a, which can be defined as follow

Consider the ionization of an acid

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

K_c is given by

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Since H_2O is in large excess, therefore its conc. is constant.

Hence

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

or

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{---} (1)$$

Where $K_c[H_2O] = K_a$ = Ionization constant of acid

Table (8.7) Dissociation constants of some acids at 25°C and their relative strength

Acid	Dissociation	K_a	Relative strength
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	Very large (10^{+7})	Very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	Very large (10^{+3})	Very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Large (10^{+3})	Very strong
HSO_4	$HSO_4 \rightleftharpoons H^+ + SO_4^{2-}$	1.3×10^{-2}	Strong
HF	$HF \rightleftharpoons H^+ + F^-$	6.7×10^{-4}	Weak
CH_3COOH	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.8×10^{-5}	Weak
H_2CO_3	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	4.4×10^{-7}	Weak
H_2S	$H_2S \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}	Weak
NH_4^+	$NH_4^+ \rightleftharpoons H^+ + NH_3$	5.7×10^{-10}	Weak
HCO_3	$HCO_3 \rightleftharpoons H^+ + CO_3^{2-}$	4.7×10^{-11}	Weak
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-16}	Very weak

Applications of ionization constant expression

- Eq (1) can be used to calculate K_a for any acid solution, if pH or $[H^+]$ of solution and initial conc. of acid [HA] dissolved is known.
- Similarly equilibrium concentration of H_3O^+ and A^- can be calculated, if initial conc. of HA and its K_a value is known.
- Strength of acid can be judged

Generally

When	$K_a < 10^{-3}$	acid is weak
	$K_a = 1$ to 10^{-3}	acid is moderately strong
	$K_a > 1$	acid is strong

- % ionization of weak acid can be calculated by the formula

$$\%\ \text{Ionazation} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \times 100$$

Ostwald's Dilution Law

It states that

Degree of dissociation of a weak electrolyte increases with increase in dilution.

Explanation

- Percentage ionization of weak acid depends upon the extent of dilution

- Generally % ionization of a weak acid increases with increase in dilution of solution (i.e. when molarity is less).

Example:

When 0.1 mole of acetic acid are dissolved in 1000 cm^3 of solution, then 1.33 molecules are dissociated out of hundred or 13.3 out of 1000. However, when 0.001 moles of acetic acid are dissolved in 1000 cm^3 of solution, then 12.6 molecules are dissociated out of 100 or 126 out of 1000.

Value of K_a remains constant at all dilutions at constant temperature.

Table (8.8) Percentage ionization and ionization constants of acetic acid at 25 °C

Molarity	% Ionization	$[H_3O^+]$	$[CH_3COOH]$	K_a
0.10000	1.33	0.001330	0.098670	1.79×10^{-5}
0.0500	1.89	0.000945	0.049060	1.82×10^{-5}
0.0100	4.17	0.000417	0.009583	1.81×10^{-5}
0.0050	5.86	0.000293	0.004707	1.81×10^{-5}
0.0010	12.60	0.000126	0.000874	1.72×10^{-5}

Example 4

What is the percentage ionization of acetic acid in a solution in which 0.1 moles of it has been dissolved / dm^3 of the solution. $Ka = 1.8 \times 10^{-5}$ *(Sargodha Board, 2011)*

Solution

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

Initial conc. (mol/dm^3): 0.1 | 0 | 0

Equilibrium conc. (mol/dm^3): $0.1 - x \approx 0.1$ (since acid is weak) | x | x

K_a for acetic acid is given by

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K_a = \frac{(x)(x)}{0.1} = 1.8 \times 10^{-5}$$

$x^2 = 0.1\ (1.8 \times 10^{-5})$

$x^2 = 1.8 \times 10^{-6}$

Taking square root on both sides

$x = 1.3 \times 10^{-3}$ moles

Hence $[H^+] = x = 1.3 \times 10^{-3}$ moles

$$\%\ \text{ionazation} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \times 100$$

$$\%\ \text{ionazation} = \frac{1.3 \times 10^{-3}}{0.1} \times 100 = \boxed{1.3\%}$$

IONIZATION CONSTANT OF BASES (K_b)

Weak bases are generally molecules or ions, which take proton from water and produce OH^- ion.

Example:

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

$$CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + OH^-{}_{(aq)}$$

Both NH_3 and CO_3^{2-} have different strength of accepting proton. The strength of bases can be expressed in terms of K_b

Consider hydrolysis of a general base

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+{}_{(aq)} + OH^-{}_{(aq)}$$

K_c is given by

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

Since H_2O is in large excess, therefore its conc. is constant

Hence

$$K_c[H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

or

$$K_b = \frac{[BH^+][OH^-]}{[B]} \quad \text{—— (1)}$$

Where $K_c[H_2O] = K_b$ = Ionization constant of base

Generally

Smaller K_b, weaker base and vice versa

Table 8.9 K_b of some important bases

Base	Dissociation	K_b	Relative strength
NaOH	$NaOH \rightleftharpoons Na^+ + OH^-$	Very high	Very strong
KOH	$KOH \rightleftharpoons K^+ + OH^-$	Very high	Very strong
$Ca(OH)_2$	$Ca(OH)_2 \rightleftharpoons 2Ca^+ + 2OH^-$	High	Strong
NH_4OH	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.81×10^{-5}	Weak
CH_3NH_2 (Methyl amine)	$CH_3NH_2 \rightleftharpoons CH_3NH_3^+ + OH^-$	4.38×10^{-4}	Weak
$C_6H_5NH_2$ Aniline)	$C_6H_5NH_2 \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.7×10^{-10}	Very weak

pK_a and pK_b

Values of K_a and K_b are generally very small numbers. These are usually written in exponential form. These can be converted to whole numbers in terms of pK_a and pK_b.

pKa is defined as the negative logarithm of Ka

i.e. $pK_a = -\log K_a$

pKb is defined as the negative logarithm of K_b

i.e. $pK_b = -\log K_b$

Example

K_a value of acetic acid is 1.8×10^{-5}. Hence its pK_a is 4.74

Results

- Larger pK_a, weaker acid and vice versa
- Larger pK_b, weaker base and vice versa
- If two acids have pK_a value difference of 1, then acid with smaller pk_a is 10 times stronger than the other. If the difference is two, then stronger acid is 100 times stronger than the weaker acid.

Exercise Q 13. (a):

What is Lowry Bronsted idea of acids and bases? Explain conjugate acids and bases.

LOWRY BRONSTED ACID AND BASES

According to Lowry–Bronsted concept of acids and bases

- ***ACID:*** It is a proton donor or have tendency to donate proton
- ***BASE:*** It is a proton acceptor or have tendency to accept proton.

Whenever a weak acid or a base is dissolved in water, a conjugate acid-base pair is produced.

Conjugate Acids and Conjugate Bases

Conjugate acid is a species, which is formed as a result of acceptance of proton by a base.

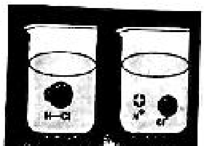
Every Bronsted acid has a conjugate base.

Conjugate base is a species, which is left behind after donation of a proton from the acid.

Example:

Ionization of HCl in water

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \longrightarrow \underset{\text{conjugate acid}}{H_3O^+} + \underset{\text{conjugate base}}{Cl^-}$$



Relationship Between Strength of Conjugate Acid-Base Pair

Consider the ionization of an acid

$$\underset{\text{(Acid)}}{HA} + \underset{\text{(Base)}}{H_2O} \rightleftharpoons \underset{\text{Conjugate acid of } H_2O}{H_3O^+} + \underset{\text{Conjugate Base of HA}}{A^-}$$

K_c is given by

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

or K_a is given by

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{—} (1)$$

Consider hydrolysis of conjugate base

$$\underset{\text{Base}}{A^-_{(aq)}} + \underset{\text{acid}}{H_2O_{(l)}} \rightleftharpoons \underset{\text{acid}}{AH_{(aq)}} + \underset{\text{base}}{OH^-_{(aq)}}$$

K_b is given by

$$K_b = \frac{[HA][OH^-]}{[A^-]} \quad \text{—} (2)$$

Multiply eq (1) and (2)

$$K_a \times K_b = \frac{[H^+][A^-]}{[HA]} \times \frac{[HA][OH^-]}{[A^-]}$$

$\therefore K_a \times K_b = [H^+][OH^-]$

$K_a \times K_b = K_w$ ____ (3)

Results

- Eq (3) shows that if K_a for an acid is known then K_b for its conjugate base can be calculated.
- Since $K_a \times K_b = K_w$
  Taking log on both sides
  $\log(K_a . K_b) = \log K_w$
  $\log K_a + \log K_b = \log K_w$
  Multiply throughout by –ve sign
  $-\log K_a - \log K_b = -\log K_w$
  $(-\log K_a) + (-\log K_b) = (-\log K_w)$
  $pK_a + pK_b = pK_w$
  Since $pK_w = 14$ at 25°C, therefore
  $pK_a + pK_b = 14$ at 25°C
- From eq (3) we have
  $K_a \times K_b = K_w$

or $K_a = \frac{K_w}{K_b}$

or $K_a \alpha \frac{1}{K_b}$

It shows that

- Stronger acid have relatively weak conjugate base, while
- Weak acid have relatively strong conjugate base

COMMON ION EFFECT

The decrease in degree of ionization of a weak electrolyte by the addition of another electrolyte having a common ion is called Common Ion Effect.

The solubility of a partially soluble electrolyte is decreased by the addition of a more soluble electrolyte having a common ion.

This decrease in solubility can be explained by Le-Chatlier's principal.

Application of Common Ion Effect

1. Precipitation Of $KClO_3$

$KClO_3$ ionizes in H_2O as

$$KClO_{3(s)} \rightleftharpoons K^+_{(aq)} + ClO_3^-{}_{(aq)}$$

If KCl is added to solution then it ionizes as follows

$$KCl_{(s)} \rightleftharpoons K^+_{(aq)} + Cl^-_{(aq)}$$

Since KCl is more soluble in H_2O than $KClO_3$, therefore, it ionizes to increase the conc of common ion(K^+). This increase, shift the $KClO_3$ dissociation equilibrium in backward direction and $KClO_3$ is precipitated.

2. Purification of NaCl

For the purification of NaCl, its saturated solution in H_2O is prepared. Through this solution HCl gas is passed

NaCl and HCl ionizes in water as

$$NaCl_{(s)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$$

$$HCl_{(g)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

HCl, due to its more solubility increases conc. of common Cl^- ions in the solution, which shift the NaCl equilibrium to left and NaCl is precipitated.

The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the conc. of unionized species increases, which come out as precipitate.

3. Salt Analysis

Common ion effect is greatly used in groups of qualitative salt analysis

I. Group II

H_2S gas ionizes as

$$H_2S_{(g)} \rightleftharpoons 2H^+_{(aq)} + S^{2-}_{(aq)}$$

In group II analysis, the concentration of S^{2-} ions is reduced by adding HCl to the solution which is more soluble.

HCl ionizes as

$$HCl_{(g)} \rightleftharpoons H^+_{(aq)} + Cl^-_{(aq)}$$

Increase in concentration of H^+ ions shift the H_2S dissociation equilibrium in backward direction and thus conc. of S^{2-} in the solution is decreased. Hence, low concentration of S^{2-} ions only precipitate group II basic radicals in salt analysis.

II. Group III

NH_4OH ionizes as

$$NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

To provide low concentration of OH^- ions, NH_4Cl is added which is more soluble.

$$NH_4Cl_{(s)} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

NH_4Cl decreases the OH^- ions conc. by suppressing ionization of NH_4OH due to common ions effect.

A mixture of NH_4Cl and NH_4OH is used as a group reagent for group III radicals in salt analysis.

4. Common ion effect is also used in qualitative analysis and the preparation of buffer.

Exercise Q17. (a) What are buffer solutions? Why do we need them in daily life?

BUFFER SOLUTIONS

A solution that resists in pH changes when small amount of an acid or a base is added to it is called buffer.

Properties of Buffer

(i) It has definite pH
(ii) Its pH is not changed on dilution
(iii) Its pH is not affected by time.
(iv) Its pH is only slightly changed when strong acids or basis are added to it.

Importance of buffer (Need for a Buffer)

- Human blood is buffered at pH 7.35. If this pH goes to 7 or 8, a person may die.
- Some reactions require specific pH. Such reactions can be carried out in a buffer of specific pH.
- Buffers are important in chemistry and in many other fields such as molecular biology, microbiology, cell biology, soil sciences, nutrition, and clinical analysis.

Exercise Q17 :

(b) How does the mixture of sodium acetate and acetic acid give us the acidic buffer?

(d) Explain that a mixture of NH_4OH and NH_4Cl gives us the basic buffer?

Preparation of Buffer

A Buffer can be prepared by following two methods.

i) Acidic buffer is prepared by mixing a weak acid and its salt with strong base
It has pH < 7.
e.g. CH_3COOH / CH_3COONa. So, this mixture gives acidic buffer.

ii) Basic buffer is prepared by mixing a weak base and its salt with strong acid
It has pH > 7
e.g. NH_4OH / NH_4Cl , So, this mixture gives basic buffer.

Buffer Action

The property of a buffer to maintain its pH, when an acid or a base is added to it, is called Buffer Action

Buffer is an application of common ion effect.

Consider the buffer of CH_3COOH / CH_3COONa.

CH_3COOH is a weak acid and ionizes very small, while CH_3COONa is a strong electrolyte and it ionizes in water to greater extent and provides acetate ions.

It decreases the ionization of CH_3COOH due to common CH_3COO^- ion and pH of solution increases.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$
$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

The buffer is actually a mixture of CH_3COOH and CH_3COO^- ions.

Table 8.10 Effect of addition of acetate ions on the pH of acetic acid solution

$[CH_3COOH]$ (mole dm^{-3})	$[CH_3COO^-]$ (mole dm^{-3})	% Dissociation	pH
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

Greater the concentration of CH_3COOH, lesser the pH of solution.

If acid or H_3O^+ ions are added to it, they react with CH_3COO^- ion to give back CH_3COOH. Thus, pH of the solution is not changed. Since acetic acid is a weak acid, it prefers to remain in unionized form.

Similarly, if a base (OH^-) is added, it reacts with H_3O^+ ions to give back H_2O. Thus pH of solution is not changed.

Similarly, basic buffer like NH_4Cl / NH_4OH resists in pH changes when acid or base is added to it.

Calculating The pH Of Buffer (Henderson's Equation)

For Acid Buffer

Consider a weak acid HA and its salt with strong base NaA. These ionizes as

$$HA \rightleftharpoons H^+ + A^-$$

$$NaA \rightleftharpoons Na^+ + A^-$$

K_a for weak acid is given by

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{—— (1)}$$

or

$$[H^+] = \frac{K_a[HA]}{[A^-]} \quad \text{—— (2)}$$

$[A^-]$ is mainly provided by NaA which is stronger electrolyte than HA. Hence, it decreases the ionization of HA.

Taking log of eq (2) on both sides

$$\log[H^+] = \log\frac{K_a[HA]}{[A^-]}$$

or

$$\log[H^+] = \log K_a + \log\frac{[HA]}{[A^-]}$$

Multiply by negative sign throughout

$$-\log[H^+] = -\log K_a - \log\frac{[HA]}{[A^-]}$$

$$pH = pK_a - \log\frac{[HA]}{[A^-]} \quad \text{—— (3)}$$

Since $[A^-]$ is mainly provided by NaA (salt), therefore it represents the conc. of salt. Thus eq (3) becomes.

$$pH = pK_a - \log\frac{[acid]}{[salt]}$$

So the Henderson's equation for acid buffer solution is

$$pH = pK_a + \log\frac{[salt]}{[acid]} \quad \text{—— (4)}$$

This equation shows that pH of acid buffer depends upon

- pKa of acid
- Concentration ratio of salt and acid

This equation can be used to prepare buffer of definite pH.

Thus by proper selecting acid and taking proper conc. of salt and acid, buffer of required pH can be prepared.

Best buffer is prepared if ratio of conc. of salt and acid are kept equal. In this case pH of the buffer is controlled by the pK_a of the acid.

Example 1

In CH_3COOH/CH_3COONa buffer

If $[CH_3COOH] = [CH_3COONa]$

Then from eq (4)

$$pH = pK_a + \log 1$$

$$pH = pK_a = 4.74$$

Example 2: Similarly for HCOOH/HCOONa buffer, if [HCOOH] = [HCOONa]

$$pH = pK_a = 3.78$$

and

if $[CH_3COOH] = 0.1\ mol\ dm^{-3}$ and $[CH_3COONa] = 1.0\ mol\ dm^{-3}$

then

$$pH = pK_a + \log\frac{[1]}{[0.1]}$$

$$pH = 4.74 + 1 = 5.74$$

Example 3 If $[CH_3COOH] = 1.0\ mol\ dm^{-3}$ and $[CH_3COONa] = 0.1\ mol\ dm^{-3}$

then

$$pH = pK_a + \log\frac{[0.1]}{[1.0]}$$

$$pH = 4.74 - 1 = 3.74$$

For Basic buffer

Consider the case of NH_4OH/NH_4Cl.

NH_4OH is a solution of NH_3 in water and can be represented as

$$NH_{3(aq)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$$

K_b is given by

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Solving this eq, we get Henderson's equation for basic buffer

$$pOH = pK_b + \log\frac{[salt]}{[base]} \quad \text{——— (5)}$$

This equation shows that pOH of basic buffer depends upon

- pK_b of base
- Concentration ratio of salt and base

Example 5

Calculate the pH of a buffer solution in which 0.11 molar CH_3COONa and 0.09 mole acetic acid solutions are present. Ka for CH_3COOH is 1.8×10^{-5} (Lahore Board, 2014)

$[CH_3COONa] = 0.11\ g/dm^3$

$[CH_3COOH] = 0.09\ g/mol$

K_a of acetic acid $= 1.8 \times 10^{-5}$

Thus $pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.74$

Hence according to Handerson's eq.

$$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH = 4.74 + \log\frac{[0.11]}{[0.09]}$$

$$pH = 4.74 + 0.087$$

$$pH = \boxed{4.83}$$

Exercise Q17 (c)

Explain OR Describe the term buffer capacity. (Faisalabad Board, 2009; Lahore Board, 2013)

Buffer Capacity

The capability of a buffer solution to maintain definite pH is called buffer capacity.

It is determined by the actual molarities of its compounds

Example

Consider CH_3COOH / CH_3COONa buffer

If $[CH_3COOH] = 0.09\ mol\ dm^{-3}$ and $[CH_3COONa] = 0.11\ mol\ dm^{-3}$

Then according to Handerson's eq

$$pH = pK_a + \log\frac{[0.11]}{[0.09]} = 4.83$$

Now if acid or base is added to this buffer solution, it will try to maintain its pH. There will be only slight change in pH.

Suppose 0.01 moles of NaOH is added to 1 dm^3 of buffer. It provides 0.01 moles of OH^- ions, which will react with 0.01 moles of H^+ ions. Thus, conc. of CH_3COOH will be decreased and conc. of CH_3COONa will be increased.

Hence remaining conc. of $CH_3COOH = 0.09 - 0.01 = 0.08\ M$

And conc. of CH_3COONa (salt) $= 0.11 + 0.01 = 0.12\ M$

$$\text{Hence } pH = pK_a + \log\frac{[0.12]}{[0.08]}$$

$$pH = 4.74 + \log\frac{[0.12]}{[0.08]} = 4.93$$

Hence pH of buffer is only slightly changed.

Addition of 0.01 moles per dm^3 of solution will change the pH from 7 to 12 in pure water.

EQUILIBRIA OF SLIGHTLY (SPARINGLY) SOLUBLE IONIC COMPOUNDS: (SOLUBILITY PRODUCT)

The product of molar concentrations of oppositely charged ions, in equilibrium with its solid salt in its saturated solution, at a given temperature is called solubility product.

It is denoted by K_{sp}

Examples and Explanation

Consider a sparingly soluble salt $PbCl_2$ dissolved in water.

$$PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + 2Cl^-_{(aq)}$$

According to law of Mass action.

$$K_c = \frac{[Pb^{2+}][Cl^-]^2}{[PbCl_2]}$$

Since $PbCl_2$ is sparingly soluble, therefore, its conc. will remain constant.

$$K_c[PbCl_2] = [Pb^{2+}][Cl^-]^2$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

where $K_c[PbCl_2] = K_{sp}$ = Solubility Product constant

Consider $PbSO_4$

$$PbSO_{4\,(s)} \rightleftharpoons Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

According to law of Mass action.

$$K_c = \frac{[Pb^{2+}][SO_4^{2-}]}{[PbSO_4]}$$

Since $PbSO_4$ is sparingly soluble, therefore, its conc. will remain constant.

$$K_c\,[PbSO_4] = [Pb^{2+}]\,[SO_4^{2-}]$$

$$K_{sp} = [Pb^{2+}][SO_4^{2-}] = 1.6 \times 10^{-8} \text{ at } 25^{\circ}C$$

Where $K_c\,[PbSO_4] = K_{sp}$ = Solubility Product

Similarly for $PbCl_2$ $K_{sp} = [Pb^{2+}][Cl^-]^2$

Value of K_{sp} is temperature dependent.

Generally K_{sp} for a sparingly soluble salt is the product of the ions, each raised to an exponent equal to the co-efficient in the balanced chemical eq.

for a general reaction.

$$A_xB_y\,(s) \rightleftharpoons xA^{y+}_{(aq)} + yB^{x-}_{(aq)}$$

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

Examples

$$CaF_{2(s)} \rightleftharpoons Ca^{2+}_{(aq)} + 2F^-_{(aq)}$$

$$K_{sp} = [Ca^{2+}][F^-]^2$$

- K_{sp} is the measure of how far to the right dissolution proceeds at equilibrium i.e saturation.
- Smaller the K_{sp}, lesser the capability to be dissociated

Table K_{sp} values for some ionic compounds (compounds are arranged alphabetically)

Salt	Ion product	K_{sp}	Salt	Ion product	K_{sp}
AgBr	$[Ag^+][Br^-]$	5.0×10^{-13}	CuS	$[Cu^{2+}][S^{2-}]$	8×10^{-34}
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	8.1×10^{-12}	FeS	$[Fe^{2+}][S^{2-}]$	6.3×10^{-18}
AgCl	$[Ag^+][Cl^-]$	1.8×10^{-10}	Fe_2S_3	$[Fe^{3+}]^2[S^{2-}]^3$	1.4×10^{-88}
AgI	$[Ag^+][I^-]$	8.3×10^{-17}	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3$	1.6×10^{-39}
Ag_2S	$[Ag^+]^2[S^{2-}]$	8×10^{-48}	HgS	$[Hg^{2+}][S^{2-}]$	2×10^{-53}
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	3×10^{-34}	$MgCO_3$	$[Mg^{2+}][CO_3^{2-}]$	3.5×10^{-8}
$BaCO_3$	$[Ba^{2+}][CO_3^{2-}]$	2×10^{-9}	$Mg(OH)_2$	$[Mg^{2+}][OH^-]^2$	6.3×10^{-10}
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	1.1×10^{-10}	MnS	$[Mn^{2+}][S^{2-}]$	3×10^{-11}
CdS	$[Cd^{2+}][S^{2-}]$	8.0×10^{-27}	$PbCl_2$	$[Pb^{2+}][Cl^-]^2$	1.6×10^{-5}
$CaCO_3$	$[Ca^{2+}][CO_3^{2-}]$	3.3×10^{-9}	$PbCrO_4$	$[Pb^{2+}][CrO_4^{2-}]$	2.3×10^{-13}
CaF_2	$[Ca^{2+}][F^-]^2$	3.2×10^{-11}	$PbSO_4$	$[Pb^{2+}][SO_4^{2-}]$	1.8×10^{-8}
$Ca(OH)_2$	$[Ca^{2+}][OH^-]^2$	6.5×10^{-6}	PbS	$[Pb^{2+}][S^{2-}]$	8.0×10^{-28}

Applications of Solubility Product

Exercise Q18 (b)

How do you determine the solubility product of a substance when its solubility is provided in grams/100 g of water?

1. Determination of K_{sp} from solubility

- If the solubility of a salt is known then its K_{sp} value can be calculated by using K_{sp} expression.
- Solubilities are given in number of grams of solute/100 g of H_2O.
- Since density of H_2O is $1\ g\ cm^{-3}$, therefore, solubility can be written as number of grams of solute/100 cm^3 of solution.
- From this amount of solute / dm^3 is calculated.
- Then amount in grams is converted into moles.
- Using balanced chemical equation, K_{sp} can be calculated

[You may write example below in LONG QUESTION as an example of Q18 (b) above]

Example 6

The solubility of PbF_2 at 25°C is 0.64 g/dm³. Calculate K_{sp} of PbF_2

(Gujranwala Board, 2011: Multan Board, 2011: Sargodha Board, 2013)

Solution

[You may write Example 6 in LONG QUESTION as an example of Q18 (b) above]

solubility of PbF_2 = 0.64 g/dm³

i.e. Mass of PbF_2 = 0.64 g

Mol. Mass of PbF_2 = 245.2 g mol⁻¹

Thus no. of moles $= \dfrac{0.64}{245.2} = 2.6 \times 10^{-3}$ moles

According to Balanced chemical eq.

	$PbF_{2(aq)} \rightleftharpoons$	$Pb^{2+}_{(aq)}$	$+\ 2F^-_{(aq)}$
At initial stage (mol/dm³)	2.6×10^{-3}	0	0
After solubility (At eqm., mol/dm³)	0	2.6×10^{-3}	$2 \times 2.6 \times 10^{-3}$

Hence $K_{sp} = [Pb^{2+}]\,[F^-]^2$

$$K_{sp} = [2.6 \times 10^{-3}]\,[2 \times 2.6 \times 10^{-3}]^2$$

$$K_{sp} = \boxed{7 \times 10^{-8}}$$

Q18 (c)

How do you calculate the solubility of a substance from the value of solubility product,

2. Determination of Solubility from K_{SP}

For this, formula of compound and K_{SP} must be known. Unknown molar solubility [S] can be calculated using balanced chemical equation.

Table: Relationship between K_{sp} and the solubility of some compounds.

Formula	No. of ions	Cation Anion	K_{sp}	Solubility $g\,dm^{-3}$
$MgCO_3$	2	1/1	3.61×10^{-8}	1.9×10^{-4}
$PbSO_4$	2	1/1	1.69×10^{-8}	1.3×10^{-4}
$BaCrO_4$	2	1/1	1.96×10^{-10}	1.4×10^{-5}
$Ca(OH)_2$	3	1/2	6.5×10^{-6}	1.175×10^{-2}
BaF_2	3	1/2	1.35×10^{-6}	7.2×10^{-3}
CaF_2	3	1/2	3.2×10^{-11}	2.0×10^{-4}
Ag_2CrO_4	3	2/1	2.6×10^{-12}	8.7×10^{-5}

Example 7

$Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is 6.5×10^{-6}. Calculate the solubility of $Ca(OH)_2$. *(Gujranwala Board, 2008; Bahawalpur Board, 2011; Lahore Board, 2014)*

Solution

K_{sp} of $Ca(OH)_2 = 6.5 \times 10^{-6}$

We know

$$Ca(OH)_{2(aq)} \rightleftharpoons Ca^{2+}_{(aq)} + 2OH^{-}_{(aq)}$$

Initial stage	$Ca(OH)_{2(aq)}$	0	0
At equilibrium	$Ca(OH)_{2(aq)}$	S	2S

Hence

$$K_{sp} = [Ca^{2+}][OH^-]^2$$

$$K_{sp} = [S][2S]^2 = 6.5 \times 10^{-6}$$

$$4[S]^3 = 6.5 \times 10^{-6}$$

$$[S] = \sqrt[3]{\frac{6.5 \times 10^{-6}}{4}}$$

or $\quad [S] = 1.175 \times 10^{-2}\ mol/dm^3$

*[You may write **Example 7** in **LONG QUESTION** as an example of **Q18 (c)** above]*

Hence at equilibrium

$[Ca^{2+}] = 1.175 \times 10^{-2}\ mol/dm^3$

and $\quad [OH^-] = 2 \times 1.175 \times 10^{-2}\ mol/dm^3$

Since

1 mole of $Ca(OH)_2$ gives 1 mole of Ca^{2+} ions, hence

Solubility of $Ca(OH)_2 = [Ca^{2+}] = \boxed{1.175 \times 10^{-2}\ mol/dm^3}$

3. *Effect of common ion on solubility*

Presence of a common ion decreases the solubility of a sparingly soluble salt

Example:

Consider saturated solution of $PbCrO_4$

$$PbCrO_{4(aq)} \rightleftharpoons Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

Now if $NaCrO_4$ is added then

$$Na_2CrO_{4(aq)} \rightleftharpoons 2Na^{+}_{(aq)} + CrO_4^{2-}{}_{(aq)}$$

Since Na_2CrO_4 is more soluble and provide common ion CrO_4^{2-}

Therefore, equilibrium of $PbCrO_4$ goes backward and its solubility is decreased.

OBJECTIVE AND SHORT ANSWER QUESTIONS (Exercise)

Q1. Multiple choice questions

(i) For which system does the equilibrium constant, K_C has units of (concentration)$^{-1}$

(a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(b) $H_2 + I_2 \rightleftharpoons 2HI$
(c) $2NO_2 \rightleftharpoons N_2O_4$
(d) $2HF \rightleftharpoons H_2 + F_2$

(Sargodha Board, 2012) (D.G. Khan Board, 2012) (Gujranwala board, 2013)

(ii) Which statement about the following equilibrium is correct

$$2SO_2 + O_2 \rightleftharpoons 2SO_3 \quad \Delta H = -188.3 \text{ kJ/mol}$$

(a) The value of K_p falls with a rise in Temperature
(b) The value of K_p falls with increasing Pressure
(c) Adding V_2O_5 catalyst increases the equilibrium yield of SO_3
(d) The value of K_p is equal to K_C

(Multan board, 2012) (Lahore board, 2013)

(iii) The pH of 10^{-3} mol/dm^3 of an aqueous solution of H_2SO_4 is

(a) 3 (b) 2.7 (c) 2 (d) 1.5

(Faisalabad Board, 2009) (D.G. Khan Board, 2012) 2013 (Lahore board, 2014)

(iv) The solubility product of AgCl is 2×10^{-10} mol^2 dm^{-6}. The maximum concentration of Ag^+ ions in the solution is

(a) 2×10^{-10} mol dm^{-3}
(b) 1.41×10^{-5} mol dm^{-3}
(c) 1×10^{-10} mol dm^{-3}
(d) 4×10^{-20} mol dm^{-3}

(Faisalabad Board, 2008) (D.G. Khan Board, 2009) (Sargodha Board, 2014)

(v) An excess of aqueous silver nitrate is added to aqueous barium chloride and precipitate is removed by filtration. What are the main ions in the filtrate?

(a) Ag^+ and NO_3^{-1} only
(b) Ag^+ and Ba^{2+} and NO_3^{-1}
(c) Ba^{2+} and NO_3^{-1} only
(d) Ba^{2+} and NO_3^{-1} and Cl^{-1}

(Gujranwala board, 2011, 2013)

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans. (c)

For the reaction

$$2NO_2 \rightleftharpoons N_2O_4.$$

Equilibrium constant expression and units of K_C are given as

$$K_C = \frac{[N_2O_4]}{[NO_2]^2} = \frac{[\text{conc.}]}{[\text{conc.}]^2} = (\text{conc.})^{-1}$$

(ii) Ans. (a)

Synthesis of SO_3 is an exothermic process. Therefore, according to Le-Chatelier's principle, increase in temperature will shift the reaction in backward direction. Hence, increase in conc. of reactants decreases the value of K_p.

(iii) Ans. (b)

H_2SO_4 is a strong acid. One molecule of H_2SO_4 gives two H^+ ions. Therefore, 10^{-3} mol dm^{-3} of H_2SO_4 gives 2×10^{-3} mol dm^{-3} of H^+ ions.

Thus $[H^+] = 2 \times 10^{-3}$

pH is calculated as

$$pH = -\log(2 \times 10^{-3}) = 2.7$$

(iv) Ans. (b)

AgCl ionizes as

	AgCl $\rightleftharpoons$	Ag^+ +	Cl^-
Initial	x	0	0
equilibrium	0	x	x

Hence

$K_{sp} = [Ag^+][Cl^-]$

or $K_{sp} = x \times x = x^2 = 2 \times 10^{-10}$

$x = \sqrt{2 \times 10^{-10}}$

$x = 1.414 \times 10^{-5}$

Hence, the concentration of $Ag^+ = 1.414 \times 10^{-5}$ mol dm^{-3}.

(v) Ans. (b)

$AgNO_3$ and $BaCl_2$ are soluble in water. When an excess of aqueous silver nitrate is added to aqueous barium chloride, then following reaction occurs

$$2AgNO_3 + BaCl_2 \longrightarrow 2AgCl + Ba(NO_3)_2$$

AgCl is water insoluble so it is removed from the solution by filtration. Since, $AgNO_3$ is added in excess, therefore all the Cl^- ions will be precipitated and removed as AgCl.

$BaNO_3$ is water soluble. It remains in the solution in the form of Ba^{2+} and NO_3^-.

Further, since excess of $AgNO_3$ is added, therefore, Ag^+ will also be present in the solution.

Hence, Ag^+, Ba^{2+} and NO_3^- will be present in the solution.

Q2. Fill in the blanks

(i) Law of mass action states that the ____ at which a reaction proceeds is directly proportional to the product of the active masses of the ____.
(ii) In an exothermic reversible reaction, ____ in temperature will shift the equilibrium towards the forward direction.
(iii) The equilibrium constant for the reaction $2O_3 \rightleftharpoons 3O_2$ is 10^{55} at 25°C, it tells that ozone is ____ at room temperature.
(iv) In a gas phase reaction, if the number of moles of reactants are equal to the number of moles of the products, K_c of the reaction is ____ to the K_p
(v) Buffer solution is prepared by mixing together a weak base and its salt with ____ or a weak acid and its salt with ____.

Answers:
(i) rate, reactants (ii) decrease (iii) unstable (iv) equal
(v) strong acid, strong base

Q3. Label the sentences True or False

(i) When a reversible reaction attains equilibrium both reactants and products are present in a reaction mixture.
(ii) The K_C of the reaction

$$A + B \rightleftharpoons C + D \quad \text{is given by}$$

$$K_C = \frac{[C][D]}{[A][B]}$$

Therefore it is assumed that [A] = [B] = [C] = [D]

(iii) A catalyst is a compound, which increases the speed of the reaction and consequently increases the yield of the product.

(iv) Ionic product K_w of pure water at 25°C is 10^{-14} $mol^2\ dm^{-6}$ and is represented by an expression
$K_w = [H^+][OH^-] = 10^{-14}\ mol^2\ dm^{-6}$

(v) AgCl is a sparingly soluble ionic solid in water. Its solution produces excess of Ag^+ and Cl^- ions.

Answers:
(i) True (ii) False (iii) False (iv) True (v) False

Q4. ***(a) Explain the terms "reversible reaction" and "state of equilibrium"***
(Lahore Board, 2012; Multan Board, 2012; Sargodha Board, 2014)

Reversible Reactions on page 431 and State of Equilibrium on page 432

(b) Define and explain the law of mass action and drive the expression for the equilibrium constant K_c.

Solved on Page 433

(c) Write K_c for the following reactions

(i) $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \rightleftharpoons Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$
(ii) $Ag^+_{(aq)} + Fe^{2+}_{(aq)} \rightleftharpoons Ag_{(s)} + Fe^{3+}_{(aq)}$
(iii) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$
(iv) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$
(v) $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

(i) $K_C = \frac{[Sn^{4+}][Fe^{2+}]^2}{[Sn^{2+}][Fe^{3+}]^2}$	(ii) $K_C = \frac{[Ag][Fe^{3+}]}{[Ag^+][Fe^{2+}]}$	(iii) $K_C = \frac{[NO]^2}{[N_2][O_2]}$
(iv) $K_C = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$	(v) $K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$	

Q5. ***(a) Reversible reactions attain the position of equilibrium, which is dynamic in nature and not static. Explain it.*** *(Sargodha Board, 2012)*

***OR** Justify that chemical equilibrium is dynamic in nature.*
(Faisalabad Board, 2009; D.G. Khan Board, 2009)

At equilibrium stage, the concentration of reactants and products become constant. Thus, there may be two possibilities.

- Either all the reactions have stopped in the system and the system becomes stationary, or
- both forward and reverse reactions are occurring at the same rate.

Second possibility is generally accepted. Hence a chemical equilibrium is called as a dynamic equilibrium.

(b) Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

It is due to two reasons.

(i) According to law of Mass Action, the rate of reaction is directly proportional to the concentration of reactants. As the reaction proceeds, the concentration of reactants decreases with time, so the rate of forward reaction decreases.

(ii) With the passage of time, the concentration of product increases, so the rate of backward reaction also increases and thus rate of forward reaction slows down.

At dynamic equilibrium state, rate of forward reaction becomes equal to the rate of backward reaction.

Q6. ***When a graph is plotted between time on X-axis and the concentration of reactants and products on Y-axis for a reversible reaction, the curve becomes parallel to time axis at a certain stage.***

(a) At what stage the curves become parallel?

The curve becomes parallel to time axis at equilibrium state. At this state,

(i) the concentration of reactants and products become constant. So, there will be no change in their concentration with time.

(ii) the rate of forward reaction becomes equal to the rate of backward reaction, so the equilibrium is dynamic in nature.

(b) Before the curves become parallel, the steepness of curves falls? Give reasons

In the beginning of reaction, the steepness of curves is more. It is because the rate of forward reaction is fast because concentration of reactant is high. With the passage of time, the concentration of reactants decreases, thus the overall rate of reaction decreases, hence steepness of curves fall until equilibrium is reached.

(c) The rate of decrease of concentrations of the reactants and rate of increase of concentrations of any of the products may or may not be equal for various types of reactions before the equilibrium time. Explain it.

Consider the following reaction

$2A + B \rightarrow 3C$

This reactions shows when 2 moles of A reacts with 1 mole of B, then 3 moles of C are produced. Thus, rate of decrease in concentration of A is twice the rate of decrease in concentration of B. Similarly, the rate of formation of C is thrice the rate of decrease in concentration of B.

So, rate of decrease in concentration of reactant or rate of increase in concentration of product depends upon the nature of reaction.

Q7. (a) Write down the relationship of different types of equilibrium constants, i.e. K_c and K_p for the following general reactions.

$$aA + bB \rightleftharpoons cC + dD$$

Solved on Page 439

(b) Decide the comparative magnitudes of K_c, K_p for the following reactions.

Synthesis of NH_3

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

K_c is given by

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

K_p is given by

$$K_p = \frac{P^2_{NH3}}{P_{N_2} \times P^3_{H2}}$$

For this reaction, change in number of moles is given by

Δn = number of moles of product – number of moles of reactants

$= 2 - (1+3) = -2$

Hence

$$K_p = K_c \times (RT)^{-2}$$

or $$K_p = K_c \times \frac{1}{(RT)^2}$$

Thus If T is such that $RT > 1$, then $K_p < K_c$

If T is such that $RT < 1$, then $K_p > K_c$

Dissociation of PCl_5

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

K_c is given by according to law of Mass Action

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

K_p is given by

$$K_p = \frac{P_{PCl3} \times P_{Cl2}}{P_{PCl5}}$$

For this reaction, change in number of moles is given by

Δn = number of moles of product – number of moles of reactants

$= 2 - 1 = 1$

$$K_p = K_c \times (RT)$$

Thus If T is such that $RT > 1$, then $K_p > K_c$

If T is such that $RT < 1$, then $K_p < K_c$

Q8. (a) Write down K_c for the following reversible reactions. Suppose that the volume of reaction mixture in all the cases is 'V' dm³ at equilibrium stage.

(i) $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

(ii) $H_2 + I_2 \rightleftharpoons 2HI$

(iii) $2HI \rightleftharpoons H_2 + I_2$

(iv) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

(v) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(b) How do you explain that some of the reactions mentioned above are affected by change of volume at equilibrium stage?

(1) The reactions in solution phase are not affected by volume changes, since, in solution $\Delta V = 0$

(2) The reactions in gas phase are of two types.

(i) the reactions in which number of moles of reactants are equal to the number of moles of products. Such, reactions are not affected by volume changes.

Example: $H_2 + I_2 \rightleftharpoons 2HI$ $\quad K_c = \frac{4x^2}{(a-x)(b-x)}$

The K_c expression for this reaction does not involve volume (V) term, so it is not affected by volume changes (or pressure changes).

(ii) the reactions in which number of moles of reactants are not equal to the number of moles of products. Such, reactions are affected by volume changes.

Example: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, $K_c = \frac{x^2}{(a-x)V}$

The K_c expression for this reaction involves, 'V' term so, it will be affected by volume changes (or pressure changes).

Q9. *Explain the following two applications of equilibrium constant. Give examples.*

(i) Direction of reaction (ii) Extent of reaction

Solved on Page 441 (Direction of Reaction) and Page 442 (Extent of Reaction)

Q10. *Explain the following with reasons.*

(a) The change of volume disturbs the equilibrium position for some of the gaseous phase reactions, but not the equilibrium constant. (Faisalabad Board, 2007; D.G. Khan Board, 2011)

The reactions in gas phase are of two types.

(i) the reactions in which number of moles of reactants are equal to the number of moles of products. Such, reactions are not affected by volume changes.

Example: $H_2 + I_2 \rightleftharpoons 2HI$

(ii) the reactions in which number of moles of reactants are not equal to the number of moles of products. Such, reactions are affected by volume changes.

Example: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, $K_c = \frac{x^2}{(a-x)V}$

The K_c expression for this reaction involves, 'V' term so, if pressure is increased then according to Le-Chatlier's principle, the reaction will proceed in backward direction to keep the constant value of K_C. Hence, equilibrium position will change but K_C will remain constant.

(b) The change of temperature disturbs both the equilibrium position and the equilibrium constant of a reaction. *(Sargodha Board, 2010; Lahore Board, 2011; Multan Board, 2012)*

The temperature change affects the enthalpy of the system. Thus, if temperature is changed, the reaction will proceed either in forward or backward direction. As a result concentration of reactants and products will change and thus value of K_C will also be changed. Hence, both equilibrium position and equilibrium constant (K_C) will be changed.

Example: $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(c) The solubility of glucose in water is increased by increasing the temperature. *(D.G. Khan Board, 2008; Gujranwala Board, 2009; Lahore Board, 2010, 2012; Faisalabad Board, 2011; Bahawalpur Board, 2012; D.G. Khan Board, 2012)*

The solubility of glucose in water is an endothermic process

$$\text{Glucose} + H_2O \rightleftharpoons \text{Glucose (aq)} \quad \Delta H = +ve$$

So, according to Le-Chatliers Principle, if temperature is increased, the system will move in forward direction. Thus, more glucose will be dissolved. Hence, solubility of glucose increases with increase in temperature.

Q11. (a) What is ionic product of water? How does this value vary with the change in T? Is it true that this value is 75 times when the T of water increased from 0°C to 100°C.

Ionic product of water is given by the equation

$K_w = [H^+][OH^-]$

Value of K_w increases with increase in temperature. It is because increase in temperature increases the ionization of H_2O. Thus, more H^+ or OH^- ions are produced. Hence value of K_w increases.

e.g.

At 25°C $K_w = 1 \times 10^{-14}$, and

At 100°C $K_w = 7.5 \times 10^{-14}$

Further

At 0°C $(K_w)_0 = 0.1 \times 10^{-14}$ ___ (1)

At 100°C $(K_w)_{100} = 7.5 \times 10^{-14}$ ___ (2)

Divide eq (2) by eq (1)

$$\frac{(K_w)_{100}}{(K_w)_0} = \frac{7.5 \times 10^{-14}}{0.1 \times 10^{-14}} = 75$$

or $\boxed{(K_w)_{100} = 75 \times (K_w)_0}$

Hence, K_w at 100°C is 75 times more than at 0°C

(b) What is the Justification for the increase of ionic product with temperature? *(Bahawalpur Board, 2008; Rawalpindi Board, 2013)*

OR *Why the K_w of water increases with increase in temperature.* *(Rawalpindi Board, 2009)*

The value of K_w increases with increase in temperature. It is because increase in temperature increases the ionization of H_2O. Thus, more H^+ or OH^- ions are produced. Hence value of K_w increases.

(d) How do you prove that at 25°C in 1dm³ of water, there are 10^{-7} moles of H_3O^+?

OR *How would you prove that at 25°C, 1 dm³ of water contains 10^{-7} moles of H_3O^+ and 10^{-7} moles of OH^-?*

At 25°C

$K_w = [H_3O^+][OH^-] = 10^{-14}$ ___ (1)

Since ionization of water gives equal number of H_3O^+ and OH^- ions, therefore

$[H_3O^+] = [OH^-]$

Hence, eq (1) can be written as

$K_w = [H_3O^+][H_3O^+] = 10^{-14}$

or $[H_3O^+]^2 = 10^{-14}$

Taking square root on both sides

$[H_3O^+] = 10^{-7}$ mol/dm³

Hence, at 25°C, water has 10^{-7} mole/dm³ of H_3O^+ ions.

Q12. (a) Define pH and pOH. How are they related with pK_w.

OR *Write down the relationship between pH, pOH and pKw*

Solved on Page 450

(b) What happens to the acidic and basic properties of aqueous solutions when pH varies from 0 to 14.

Solved on Page 451

(c) Is it true that the sum of pK_a and pK_b is always equal to 14 at all temperatures for any acid? If not why? *(D.G. Khan Board, 2011)*

The sum of pK_a and pK_b is equal to 14 only at 25°C since pK_w = 14 at 25°C. If the temperature is increased then ionization of water also increases. Thus, value of K_w increases

and pK_w decreases (since $pKw \propto \frac{1}{K_w}$). Thus, at other temperatures, the sum of pK_a and pK_b is not equal to pKw. Since, Kw increases with temperature, therefore, value of pK_w is less than 14 at temperatures higher than 25°C.

Q 13. (a) *What is Lowry Bronsted idea of acids and bases? Explain conjugate acids and bases.*

OR *Define acid and base by Lowry-Bronsted concept.* (Rawalpindi Board, 2013)

Solved on Page 456

(b) Acetic acid dissolves in water and gives proton to water, but when dissolves in H_2SO_4, it accepts proton. Discuss the role of acetic acid in both cases. (Sargodha Board, 2009)

Acetic acid is a stronger acid than water. So, it donates proton to water and acts as an acid.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

However, H_2SO_4 is a stronger acid than acetic acid. Therefore, H_2SO_4 donates proton and acts as an acid while acetic acid accepts proton and acts as a base.

$$H_2SO_4 + CH_3COOH \rightleftharpoons HSO_4^- + CH_3COOH_2^+$$

Q14. In the equilibrium $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ $\Delta H = 90$ kJ/mol

What is the effect on

(a) The position of equilibrium (b)Equilibrium constant? If

(i) Temperature is increased

The reaction is exothermic. Therefore, according to Le-Chatlier's principle, increase in temperature favours forward reaction. Thus, concentration of PCl_5 will decrease and that of PCl_3 and Cl_2 will increase. Hence, it will disturb both equilibrium position and equilibrium constant (K_C) of the reaction.

(ii) Volume of the container is decreased.

In this reaction, numbers of moles of reactants are less than that of product. Therefore, according to Le-Chatliers principle, decrease in volume favours backward reaction towards less volume. This will change the equilibrium position but value of Kc remains constant.

(ii) Catalyst is added

The catalyst has no effect on the equilibrium composition of the system. Thus, it will not affect both equilibrium position and K_C. It simply increases the rate of forward and backward reaction. Thus, it only decreases the time to reach the equilibrium state.

(iv) Cl_2 is added

Cl_2 is the product of reaction. Therefore, according to Le-Chatlier's principle, adding Cl_2 favours backward direction. In this case, equilibrium position will be changed but the value of K_C will remains constant.

Q15. Synthesis of NH_3 by Haber's process is an exothermic reaction.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.46 \text{ kJ/mol}$$

(a) What should be the possible effect of change of temperature at equilibrium stage?

Since reaction is exothermic, hence according to Le-chatliers principle, decrease in temperature favours forward reaction. The optimum temperature is 400°C.

(b) How does the change of pressure or volume shifts the equilibrium position of this reaction?

OR *What will be the effect of change in pressure on ammonia synthesis?* **(Lahore Board, 2007; Faisalabad Board, 2008; Multan Board, 2010; Gujranwala Board, 2014)**

OR *How does the change of pressure shifts the equilibrium position of synthesis of ammonia* **(Lahore Board, 2012)**

Since number of moles of products is less than number of moles of reactants. Therefore, according to Le-Chatliers principle, increase in pressure decreases the volume and thus favours forward reaction towards less volume. The optimum pressure is 200-300 atm.

(c) What is the role of the catalyst in this reaction?

The catalyst used in this reaction consists of pieces of iron embedded in a fused mixture of MgO, Al_2O_3 and SiO_2. It simply increases the rate of forward and backward reaction. Thus, it decreases the time to reach the equilibrium state.

(d) What happens to equilibrium position of this reaction if NH_3 is removed from the reaction vessel from time to time.

According to Le-Chatliers Principle, by continuous removal of NH_3 from the reaction mixture, reaction moves in forward direction.

Q16. Sulphuric acid is the king of chemicals. It is produced by the burning of SO_2 to SO_3 through an exothermic reversible process.

(a) Write the balanced reversible reaction

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} \quad \Delta H = -194 \text{ kJ/mol}$$

(b) What is the effect of pressure change on this reaction?

Since number of moles of products is less than number of moles of reactants. Therefore, according to Le-Chatliers principle, increase in pressure decreases the volume and thus favours forward reaction towards less volume.

(c) Reaction is exothermic but still the temperature of 400–500°C is required to increase the yield of SO_3. Give reasons.

Since reaction is exothermic, hence according to Le-chatliers principle, decrease in temperature favours forward reaction and the yield of SO_3 is increased. However, at low temperature, the rate of formation of SO_3 is slow. To increase the rate an optimum temperature of 400 – 500°C is used.

Q17. (a) What are buffer solutions? Why do we need them in daily life?

Solved on Page 460

(b) How does the mixture of sodium acetate and acetic acid give us the acidic buffer?

Solved on Page 461

(d) Explain that a mixture of NH_4OH and NH_4Cl gives us the basic buffer?

(Rawalpindi Board, 2010, 2011: Multan Board, 2012: Sargodha Board, 201...)

Solved on Page 461

(d) How do you justify that the greater quantity of CH_3COONa in acetic acid decreases the dissociating power of acetic acid and so the pH increases.

OR When the concentration of salt is increased in an acidic buffer, then the pH of the solution increases. Why? (Lahore Board, 20...)

CH_3COOH is a <u>weak acid</u> and ionizes very small, while CH_3COONa is a strong <u>electrolyte</u> and it ionizes in water to greater extent and provides acetate ions.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

Thus, CH_3COONa <u>decreases</u> the ionization of CH_3COOH due to common CH_3COO^- ion and pH of solution <u>increases</u>.

(e) Explain OR Describe the term buffer capacity. (Faisalabad Board, 2009: Lahore Board, 20...)

Solved on Page 464

Q18. (a) What is the solubility product? Derive the solubility product expression for sparingly soluble compounds, $AgCl$, Ag_2CrO_4 and $PbCl_2$.

OR Define solubility product. Derive solubility product expression for Ag_2CrO_4 and $PbCl_2$. (Sargodha Board, 20...)

Solved on Page 465

(b) How do you determine the solubility product of a substance when its solubility is provided in grams/100 g of water?

OR How can you determine K_{sp} from solubility? (Faisalabad Board, 2012)

Solved on Page 467

(c) How do you calculate the solubility of a substance from the value of solubility product.

Solved on Page 468

IMPORTANT FORMULAS

$pH = -\log[H^+]$, $pOH = -\log[OH^-]$, $pK_a = -\log K_a$, $pK_b = -\log K_b$, $pK_w = -\log K_w$

$pH + pOH = 14$, $pK_a + pK_b = pK_w$, $K_a \times K_b = K_w$

$$\%\text{ionization of an acid or a base} = \frac{\text{Amount of substance ionized}}{\text{Amount of substance initially available}} \times 100$$

<u>Henderson's equation</u>

For an acid buffer $pH = pK_a + \log\frac{[salt]}{[acid]}$, and for a basic buffer $pOH = pK_b + \log\frac{[salt]}{[base]}$

NUMERICAL PROBLEMS (Exercise)

Q19. Kc value for volume for the following reaction is 0.016 at 520°C

$$2HI \rightleftharpoons H_2 + I_2$$

Equilibrium mixture contains [HI] = 0.08 M, [H₂] = 0.01 M, [I₂] = 0.01 M. To the mixture more HI is added so that its new concentration is 0.096 M. what will be the concentration of [HI], [H₂] and [I₂] when equilibrium is re-established.

Solution

	$2HI \rightleftharpoons$	H_2	$+ I_2$
Equilibrium conc. (mol/dm³)	0.08	0.01	0.01
Initial conc. after adding more HI (mol/dm³)	0.096	0.01	0.01
Equilibrium conc. When equilibrium is re-established (mol/dm³)	0.096 − 2x	0.01 + x	0.01 + x

According to law of mass action

$$K_c = \frac{[H_2][I_2]}{[HI]^2}$$

$$K_c = \frac{(0.01+x)(0.01+x)}{(0.096-2x)^2} = 0.016$$

$$= \frac{(0.01+x)^2}{(0.096-2x)^2} = 0.016$$

Taking square root on both sides

$$\sqrt{\frac{(0.01+x)^2}{(0.096-2x)^2}} = \sqrt{0.016}$$

$$\frac{(0.01+x)}{(0.096-2x)} = 0.126$$

$$0.01+x = 0.126\,(0.096-2x)$$

$$0.01+x = 0.0121 - 0.252\,x$$

$$x + 0.252\,x = 0.0121 - 0.01$$

$$1.252\,x = 0.0021$$

$$x = \frac{0.0021}{1.252}$$

$$x = 0.00168 \text{ mol dm}^{-3}$$

Thus

Concentrations when equilibrium is re-established are

$$[H_2] = 0.01 + x = 0.01 + 0.00168 = \boxed{0.01168 \text{ mol dm}^{-3}}$$

$$[I_2] = 0.01 + x = 0.01 + 0.00168 = \boxed{0.01168 \text{ mol dm}^{-3}}$$

$$[HI] = 0.096 - 2x = 0.096 - 2 \times 0.00168 = \boxed{0.0926 \text{ mol dm}^{-3}}$$

Q20. The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4. A mixture of 3 moles of acetic acid and one mole of C_2H_5OH is allowed to come to equilibrium. Calculate the amount of ethyl acetate at equilibrium stage in number of moles and grams. Also calculate the masses of reactants left behind.

Solution

	CH_3COOH	$+ C_2H_5OH \rightleftharpoons$	$CH_3COOC_2H_5$	$+ H_2O$
Initial conc. (mol/dm³)	3	1	0	0
Equilibrium conc. (mol/dm³)	3 − x	1 − x	x	x

According to law of mass action

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

$$K_c = \frac{(x)(x)}{(3-x)(1-x)} = 4$$

$$x^2 = 4\,(3-x)\,(1-x)$$

$$x^2 = 4\,(3 - 3x - x + x^2)$$

$$x^2 = 4\,(3 - 4x + x^2)$$

$$x^2 = 12 - 16x + 4x^2$$

or $12 - 16x + 4x^2 - x^2 = 0$

$$3x^2 - 16x + 12 = 0$$

It is a quadratic equation and can be solved by using quadric formula

Here $a = 3$, $b = -16$, $c = 12$

Thus

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(-16) \pm \sqrt{(-16)^2 - 4(3)(12)}}{2(3)}$$

$$x = \frac{16 \pm \sqrt{256 - 144}}{6}$$

$$x = \frac{16 \pm \sqrt{112}}{6}$$

$$x = \frac{16 \pm 10.58}{6}$$

Either $x = \frac{16+10.58}{6}$ or $x = \frac{16-10.58}{6}$

$x = 4.43\ mol\ dm^{-3}$ or $x = 0.9\ mol\ dm^{-3}$

$x=4.43$ is not possible as it is greater than the initial concentrations of reactants, therefore, $x=0.9\ mol\ dm^{-3}$

Therefore

Moles of ethyl acetate	$= x = 0.9$ moles
Mass of ethyl acetate	$= 0.9 \times 88 = \boxed{79.46\ g}$
Moles of water	$= x = 0.9$ moles
Mass of water	$= 0.9 \times 18 = \boxed{16.2\ g}$
Moles of acetic acid (left behind)	$= 3 - x = 3 - 0.9 = 2.1$ moles
Mass of acetic acid (left behind)	$= 2.1 \times 60 = \boxed{126\ g}$
Moles of ethyl alcohol (left behind)	$= 1 - x = 1 - 0.9 = 0.1$ moles
Mass of ethyl alcohol (left behind)	$= 0.1 \times 46 = \boxed{4.6\ g}$

Q21. *Study the equilibrium*

$$H_2O + CO \rightleftharpoons H_2 + CO_2$$

(a) Write an expression of K_p

$$K_P = \frac{P_{H_2} \times P_{CO_2}}{P_{H_2O} \times P_{CO}}$$

(b) When 1 mole of steam and 1 mole of CO are allowed to reach equilibrium, 33.3% of the equilibrium mixture is hydrogen. Calculate the value of K_p. State the units of K_p

Solution

	H_2O +	CO ⇌	H_2 +	CO_2
Initial conc. (mol/dm³)	1	1	0	0
Equilibrium conc. (mol/dm³)	$1-x$	$1-x$	x	x

Total no. of moles at equilibrium $= 1 - x + 1 - x + x + x = 2$

Hence

$$\%\ of\ H_2 = \frac{\text{no of moles of } H_2}{\text{total no. of moles}} \times 100$$

$$33.3 = \frac{\text{no of moles of } H_2}{2} \times 100$$

or no of moles of $H_2 = \frac{33.3}{100} \times 2 = 0.67$ moles

Hence

At equilibrium

Moles of H_2	$= x = 0.67$ moles
Moles of CO_2	$= x = 0.67$ moles
Moles of H_2O	$= 1 - x = 1 - 0.67 = 0.33$ moles
Moles of CO	$= 1 - x = 1 - 0.67 = 0.33$ moles

Hence, K_c is given as

$$K_c = \frac{[H_2] \times [CO]}{[H_2O] \times [CO_2]}$$

$$K_c = \frac{0.67 \times 0.67}{0.33 \times 0.33} = 4$$

Since $K_p = K_c (RT)^{\Delta n}$ and $\Delta n = n_{products} - n_{reactants} = 0$, therefore

$$\boxed{K_p = K_c = 4}$$

Q22. *Calculate the pH of*

(a) 10^{-4} moles/dm³ of HCl (Gujranwala Board, 2010)

HCl ionizes as

$$HCl \rightleftharpoons H^+ + Cl^-$$

Since HCl is a strong acid, and it is 100% dissociated. Hence $10^{-4}\ mol/dm^3$ of HCl produces $10^{-4}\ mol/dm^3$ of H^+ ions.

Thus

$[H^+] = 10^{-4}\ mol/dm^3$

So

$$pH = -\log[H^+]$$
$$pH = -\log(10^{-4})$$
$$pH = \boxed{4}$$

(b) 10^{-4} moles/dm³ of $Ba(OH)_2$

$Ba(OH)_2$ ionizes as

$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$$

Since $Ba(OH)_2$ is a strong base and it is 100% dissociated.
Hence 10^{-4} mol/dm^3 of $Ba(OH)_2$ produces 2×10^{-4} mol/dm^3 of OH^- ions.

Thus
$[OH^-] = 2 \times 10^{-4}$ mol/dm^3
So
$pOH = -\log[OH^-]$
$pOH = -\log[2 \times 10^{-4}]$
$pOH = 3.699$
Since
$pH + pOH = 14$

Therefore
$pH = 14 - pOH$
$= 14 - 3.699 = \boxed{10.301}$

(c) 1 mol/dm^3 of H_2X, which is 50%, dissociated (Faisalabad Board, 2013)

H_2X ionizes as
$$H_2X \rightleftharpoons 2H^+ + X^-$$
1 mole of H_2X produces 2 moles of H^+ ions if 100% dissociated.
However, since H_2X is 50% dissociated therefore 1 mole of H_2X produces 1 mole of H^+ ion.
Thus
$[H^+] = 1$ mol/dm^3
So
$pH = -\log[H^+]$
$pH = -\log[1]$
$pH = \boxed{0}$

(d) 1 mol/dm^3 of NH_4OH which is 1% dissociated

NH_4OH ionizes as
$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
It shows that 1 mole of NH_4OH produces 1 mole of OH^- ions.
NH_4OH is only 1% dissociated.
Hence

$$\%\ \text{dissociation} = \frac{\text{mol of } OH^-}{\text{total moles of } NH_4OH} \times 100$$

$$1 = \frac{\text{mol of } OH^-}{1} \times 100$$

$$\text{mol of } OH^- = \frac{1}{100} \times 1 = 0.01 \text{ mol/dm}^3$$
Thus
$[OH^-] = 0.01$ mol/dm^3
So
$pOH = -\log[OH^-]$
$pOH = -\log[0.01]$
$pOH = 2$
Since
$pH + pOH = 14$
Therefore
$pH = 14 - pOH$
$= 14 - 2 = \boxed{12}$

Q23. (a) Benzoic acid C_6H_5COOH is a weak mono-basic acid ($Ka = 6.4 \times 10^{-5}$ mol/dm^3). What is the pH of a solution containing 7.2 g of sodium benzoate in one dm^3 of 0.02 mol/dm^3 benzoic acid. (Sargodha Board, 2013)

Mass of sodium benzoate $= 7.2$ g / dm^3
Mol. Mass of sodium benzoate $= 144$ g/mol

Formula of sodium benzoate is C_6H_5COONa

Moles of sodium benzoate $= \frac{7.2}{144} = 0.05$ mol/dm^3
Moles of benzoic acid $= 0.02$ mol/dm^3
K_a of benzoic acid $= 6.4 \times 10^{-5}$ mol/dm^3
Thus $pK_a = -\log K_a = -\log(6.4 \times 10^{-5}) = 4.2$

Hence, according to Henderson's eq.
$$pH = pK_a + \log\frac{[\text{sodium benzoate}]}{[\text{benzoic acid}]}$$
$$pH = 4.2 + \log\frac{[0.05]}{[0.02]}$$
$pH = 4.2 + 0.39$
$pH = \boxed{4.59}$

(b) A buffer solution has been prepared by mixing 0.2 M CH_3COONa and 0.5 M CH_3COOH in 1 dm^3 of solution. Calculate the pH of solution. pK_a of acid is 4.74 at 25°C. How the value of pH will change by adding 0.1 mole of NaOH and 0.1 mole of HCl respectively.

Solution

$[CH_3COOH] = 0.5$ M
$[CH_3COONa] = 0.2$ M
pKa of $CH_3COOH = 4.74$

pH = ?

Since $pH = pK_a + \log\frac{[Salt]}{[Acid]}$

or $pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$

$pH = 4.74 + \log\frac{[0.2M]}{[0.5M]}$

$pH = 4.74 - 0.4$

$pH = \boxed{4.34}$

When 0.1 mole of NaOH is added

NaOH is a strong base. It dissociates completely. Therefore, it produces 0.1 moles of OH^- ions. Thus, 0.1 moles of OH^- ions reacts with 0.1 moles of CH_3COOH. Hence, out of 0.5 moles of CH_3COOH, 0.4 moles of CH_3COOH are left behind.

On the other hand, due to salt formed by the neutralization reaction, conc. of salt (CH_3COONa) is increased from 0.2 moles to 0.3 moles.

Hence, new conc. will be

$[CH_3COOH] = 0.4\ M$ $[CH_3COONa] = 0.3\ M$

Thus $pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$

$pH = 4.74 + \log\frac{[0.3]}{[0.4]}$

$pH = 4.74 - 0.12$

$pH = 4.62$

Addition of 0.1 mole of HCl

HCl is a strong acid. It dissociates completely. Therefore, it produces 0.1 moles of H^+ ions. Thus, 0.1 moles of H^+ ions react with 0.1 moles of CH_3COO^- ions. Hence, out of 0.2 moles of salt ($CH_3COO^-Na^+$), 0.1 moles of salt are left behind.

On the other hand, conc. of acid (CH_3COOH) is increased from 0.5 moles to 0.6 moles.

Hence, new conc. will be

$[CH_3COOH] = 0.6\ M$ $[CH_3COONa] = 0.1\ M$

Thus $pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$

$pH = 4.74 + \log\frac{[0.1]}{[0.6]}$

$pH = 4.74 - 0.78$

$pH = \boxed{3.96}$

(See Section 8.7.1 for complete understanding of this numerical)

Q24. *Solubility of CaF_2 in water at 25°C is found to be 2.05×10^{-4} mol dm^{-3}. What is the value of K_{sp} at this temperature.* *(Gujranwala Board, 2009, 2013)*

Solubility of $CaF_2 = 2.05 \times 10^{-4}$ mol dm^{-3}

According to Balanced chemical eq.

	$CaF_{2(s)} \rightleftharpoons$	$Ca^{2+}_{(aq)}$	$+ 2F^-_{(aq)}$
At initial stage (mol/dm^3)	2.05×10^{-4}	0	0
After solubility (At eq. mol/dm^3)	0	2.05×10^{-4}	$2 \times 2.05 \times 10^{-4}$

Hence $K_{sp} = [Ca^{2+}][F^-]^2$

$K_{sp} = [2.05 \times 10^{-4}][2 \times 2.05 \times 10^{-4}]^2$

$K_{sp} = \boxed{3.446 \times 10^{-11}\ mol^3\ dm^{-9}}$

Q25. *The solubility product of Ag_2CrO_4 is 2.6×10^{-2} at 25°C. Calculate the solubility of the compound.*

K_{sp} of $Ag_2CrO_4 = 2.6 \times 10^{-2}$

We know

	$Ag_2CrO_{4(s)} \rightleftharpoons$	$2Ag^+_{(aq)} + CrO_4^{2-}{}_{(aq)}$	
Initial stage (mol/dm^3)	Ag_2CrO_4	0	0
At equilibrium (mol/dm^3)	Ag_2CrO_4	2S	S

Hence

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$

$K_{sp} = [2S]^2[S] = 2.6 \times 10^{-2}$

$4[S]^3 = 2.6 \times 10^{-2}$

$[S] = \sqrt[3]{\frac{2.6\times10^{-2}}{4}}$

or $[S] = 0.1866$ mol/dm^3

Hence at equilibrium

$[Ag^+] = 2 \times 0.1866$ mol/dm^3 = 0.3732 mol/dm^3

and $[CrO_4^{2-}] = 0.1866$ mol/dm^3

Since

1 mole of Ag_2CrO_4 gives 1 mole of CrO_4^{2-} ions, hence

Solubility of $Ag_2CrO_4 = [CrO_4^{2-}] = \boxed{0.1866\ mol/dm^3}$

HELLO! Mr. Question here!

OBJECTIVE: Multiple Choice Questions from PAST PAPERS

1. The pH of human blood is: *(Rawalpindi board, 2011)*
   (a) 8.0 (b) 7.53 (c) 7.63 (d) 7.35
2. When HCl is added to aqeous solution of H_2S, its ionization: *(Rawalpindi board, 2011)*
   (a) Increases (b) Remains constant
   (c) Decreases (d) First decreases then increases
3. The pH of 10^{-3} mol dm^{-3} of an aqueous solution of *HCl* is: *(Rawalpindi board, 2012)*
   (a) 1.5 (b) 2.0 (c) 3.0 (d) 2.7
4. The pH of human blood is: *(Gujranwala board, 2010)*
   (a) 7.0 (b) 4.0 (c) 6.5 (d) 7.4
5. The ionic product of water will increase if: *(Gujranwala board, 2010)*
   (a) H^+ ions are added (b) OH^- ions are added
   (c) temperature is increased (d) pressure is increased
6. Ionic product of water (K_w) increases when temperature increases form 0°C to 100°C *(Lahore board, 2013)*
   (a) 25 times (b) 75 times (c) 55 times (d) 65 times
7. When K_c value is small, the equilibrium position is: *(Gujranwala board, 2008)*
   (a) towards left(b) towards right (c) remains unchanged (d) none of these
8. A basic buffer solution can be prepared by mixing *(Gujranwala board, 2008)*
   (a) strong acid and its salt with weak strong acid
   (b) weak base and its salt with strong acid
   (c) strong base and its salt with weak acid
   (d) weak acid and its salt with strong base
9. Which salt dissolved in water forms a solution with a pH greater than 7 *(Gujranwala board, 2009)*
   (a) NaCl (b) $CuSO_4$ (c) Na_2CO_3 (d) NH_4Cl
10. The pOH of solution is 4. The H^+ ion concentration of solution is: *(Gujranwala board, 2012)*
    (a) 4.0 moles/dm^3 (b) 10^{-10} moles/dm^3
    (c) 0.4 moles/dm^3 (d) 4 × 104 moles / dm^3
11. The solubility of $KC\ell O_3$ in water is suppressed by adding: *(Multan board, 2011)*
    (a) $NaC\ell O_3$ (b) $NaC\ell$ (c) $KMnO_4$ (d) $KC\ell$
12. The tem pH was introduced by: *(Multan board, 2011)*
    (a) Henderson (b) Sorenson (c) Goldsmith (d) Thomson
13. pH of a buffer can be calculated by using: *(Multan board, 2011)*

    (a) Moseley's equation (b) Henderson's equation
    (c) De-Broglie's equation (d) Bohr's equation
14. In synthesis of Ammonia by Haber's process, the optimum condition for pressure is: *(Multan board, 2011)*
    (a) 150 – 160 atm (b) 170 – 200 atm (c) 200 – 300 atm (d) 300 – 350 atm
15. Common Ion effect finds extensive application in: *(Gujranwala board, 2014)*
    (a) Quantitative analysis (b) Qualitative analysis
    (c) Spectroscopic Analysis (d) Thermal analysis
16. Dissociation of H_2S in water can be suppressed by the addition of: *(Gujranwala board, 2014)*
    (a) $HC\ell$ (b) $NH_4C\ell$ (c) NH_4OH (d) $NaOH$
17. The pH of human blood is *(Multan board, 2013)*
    (a) 7.32 (b) 7.33 (c) 7.34 (d) 7.35
18. $pH = pKa + \log [Salt] / [Acid]$ is known as *(Multan board, 2013)*
    (a) Einstein equation (b) Planck equation
    (c) Gibb's equation (d) Handerson equation
19. For the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$
    (a) $K_c = K_p$ (b) $K_c < K_p$ (c) $K_c > K_p$ (d) $K_c = K_p$
    ________ million Tons ammonia is produced by Haber's Process?
    (a) 110 (b) 120 (c) 115 (d) 200
20. The concentrations of reactants and products at equilibrium are:
    (a) Equal (b) Maximum (c) Minimum (d) Constant
    (Lahore Board, 2009)
21. The value of equilibrium constant can predict: *(Bahawalpur Board, 2009)*
    (a) The direction of reaction (b) The extent of reaction
    (c) The effect of catalyst used (d) Both the direction and extent of reaction
22. For acidic solution, pH will be *(Sargodha Board, 2009)*
    (a) 7 (b) less than 7 (c) grater than 7 (d) zero
23. The pH of a solution is 9, the solution is *(Rawalpindi Board, 2009)*
    (a) weak acid (b) Weak base (c) Strong acid (d) Strong base
24. Law of mass action derived by Guldberg and Waag in *(Lahore Board, 2010)*
    (a) 1909 (b) 1906 (c) 1846 (d) 1864
25. Which relationship is correct about the strength of an acid with the strength of its conjugated base? *(Lahore Board, 2010)*
    (a) $K_a \propto \frac{1}{K_b}$ (b) $K_a \propto K_b$ (c) $K_a \propto \sqrt{K_a}$ (d) None of these

26. The aqueous solution of $BiCl_3$ is cloudy. The cloudiness of $BiCl_3$ solution can be cleared by *(Lahore Board, 2010)*
    (a) additional of $BiCl_3$ (b) Addition of H_2O
    (c) Addition of HCl (d) Addition of $BiCl_3$ and H_2O
27. Ionization of hydrogen sulphide gas is suppressed by: *(Lahore Board, 2010)*
    (a) KCl (b) NaCl (c) HCl (d) $KClO_3$
28. The unit of equilibrium constant K_c for the reaction. *(Multan board, 2010)*
    $H_2 + I_2 \rightleftharpoons 2HI$ is:
    (a) $mole^{-1}\ dm^3$ (b) $mole^{-2}\ dm^3$ (c) $mole\ dm^{-1}$ (d) none of these
29. Which of the following reactions will be favoured to the forward directions at low pressure? *(Multan board, 2010)*
    (a) $N_2 + O_2 \rightleftharpoons 2NO$ (b) $N_2 + 3H_2 \rightleftharpoons 2nH_3$
    (c) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (d) $H_2 + I_2 \rightleftharpoons 2HI$
30. High value of Ka means that acid is *(Sargodha Board, 2010)*
    (a) very weak (b) weak (c) strong (d) very strong
31. In Haber process, for formation of NH_3, the pressure used is *(Sargodha Board, 2010)*
    (a) 100 atm (b) 200 – 300 atm (c) 600 atm (d) 1000 atm
32. The pH of 10^{-3} mol dm^{-3} of an aqueous solution of HCl is *(Bahawalpur Board, 2010)*
    (a) 3.0 (b) 2.7 (c) 2.0 (d) 1.5
33. If NaOH is added to a solution of CH_3COOH then *(Rawalpindi Board, 2010)*
    (a) pH of solution decreases
    (b) H^+ ions concentration increase
    (c) CH_3COO^- ions concentration increase
    (d) CH_3COOH ions concentration increase
34. The law of mass actin was given by *(Rawalpindi Board, 2010)*
    (a) Van't Hoff (b) Bodeinstin
    (c) Guldberg and Waage (d) Berthelot
35. pH of rain water is *(D.G. Khan Board, 2010)*
    (a) 5 (b) 6.0 (c) 6.2 (d) 7.0
36. Equilibrium constant for gaseous equilibrium is represented by *(D.G. Khan Board, 2010)*
    (a) K_c (b) K_c (c) K_x (d) K_p
37. The term pH was introduced by *(Lahore Board, 2011)*
    (a) Hendersen (b) Sorensen (c) Goldstein (d) Thomson
38. The relationship between Kp and Kc is given by *(Lahore Board, 2011)*

(a) $K_c = K_p (P)^{\Delta n}$ (b) $K_c = K_p \left(\frac{P}{N}\right)^{\Delta n}$

(c) $K_p = K_c (RT)^{\Delta n}$ (d) $K_p = K_c (RT)^{-\Delta n}$

39. The units for K_w of H_2O are. *(Faisalabad Board, 2011)*
    (a) moles dm^{-3} (b) $moles^2 . dm^{-6}$ (c) $moles^{-2} dm^6$ (d) $moles^{-2} . dm^{-3}$
40. The pH of mixture of CH3COONa and CH3COOH is *(Faisalabad Board, 2011)*
    (a) 7 (b) > 7 (c) < 7 (d) 1
41. The sum of pH and pOH is always *(Lahore Board, 2007)*
    (a) 7 (b) Zero (c) 14 (d) 10^{14}
42. In case when $[OH^-] > [H^+]$ the solution is *(Faisalabad Board, 2007)*
    (a) Acidic (b) Neutral (c) Basie (d) None of these
43. By adding NH_4Cl to NH_4OH solution. The ionization of NH_4OH *(Sargodha Board, 2013)*
    (a) increases (b) remains same (c) decreases (d) increases 100 times
44. Reaction of $BiCl_3$ with H_2O gives white ppt. of BiOCl and HCl is formed. The white ppt. disappears by *(Sargodha Board, 2011)*
    (a) adding $BiCl_3$ (b) adding HCl
    (c) increasing temperature (d) decreasing temperature

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(d)	2	(c)	3	(c)	4	(c)	5	(b)
6	(a)	7	(b)	8	(c)	9	(b)	10	(d)
11	(b)	12	(b)	13	(c)	14	(b)	15	(a)
16	(d)	17	(d)	18	(b)	19	(a)	20	(d)
21	(d)	22	(b)	23	(b)	24	(d)	25	(a)
26	(c)	27	(c)	28	(d)	29	(c)	30	(d)
31	(b)	32	(a)	33	(c)	34	(c)	35	(a)
36	(d)	37	(b)	38	(c)	39	(b)	40	(c)
41	(c)	42	(c)	43	(c)	44	(b)		

SHORT & LONG QUESTIONS FROM PAST PAPERS

HESS'S LAW OF CONSTANT HEAT SUMMATION, BORN-HABER CYCLE

Short Questions

Short Questions: (S1 means Short Question 1, etc.)

Justify that one molal solution of urea in water is dilute .. (Bahawalpur Board, 2009)

How the solution of copper sulphate is acidic in nature? (Sargodha Board, 2009)

$Na_2SO_4.10H_2O$ shows discontinuous solubility curve. Give reason. (Sargodha Board, 2013)

Why aqueous solution of NH_4Cl is acidic but that of CH_3COOH is basic? (Rawalpindi Board, 2013)

Calculate pH of 10^{4} mol/dm^3 of $Ba(OH)_2$

Aqueous solution of Na_2CO_3 is alkaline in nature. Explain. (D.G. Khan Board, 2007)

REVERSIBLE, IRREVERSIBLE REACTIONS, CHEMICAL EQUILIBIUM

Short Questions

Short Questions: (S1 means Short Question 1, etc.)

(1) Define reversible and irreversible reactions. Give examples. (Azad Kashmir Board, 2012)

(2) Differentiate between reversible and irreversible reactions. Give examples. (Rawalpindi Board, 2011; D.G. Khan Board, 2012)

(3) Define state of chemical equilibrium. OR what do you understand by chemical equilibrium? (Gujranwala Board, 2008; D.G. Khan Board, 2012)

LAW OF MASS ACTION

Short Questions

(1) Define law of mass action. (Multan Board, 2007; D.G. Khan Board, 2012; Sargodha Board, 2014)

(2) Why the equilibrium constant value has its units for some of the reversible reactions, but has no units for some other reactions? (D.G. Khan Board, 2008; Rawalpindi Board, 2013)

Long Questions

(1) Define law of mass action. Derive equilibrium constant expression for a general chemical reaction. (Sargodha Board, 2011; Multan Board, 2012)

EQUILIBRIUM CONSTANT EXPRESSIONS

Short Questions

(1) Derive K_c expression for the reaction. (Lahore Board, 2008)

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(2) Derive equilibrium constant expression for the dissociation of PCl_5 (Multan Board, 2009, 2011)

(3) Write equilibrium constant expression for the reaction. (Bahawalpur Board, 2010)

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(4) Write down relation between K_c and K_p (D.G. Khan Board, 2012) OR What are Kp and Kc and how these are related? (Gujranwala Board, 2012)

APPLICATION OF EQUILIBRIUM CONSTANT

Short Questions

(1) How K_c predict the extent of a chemical reaction? (Faisalabad Board, 2011; Rawalpindi Board, 2013)

(2) Write two applications of equilibrium constant. (Gujranwala Board, 2011; Lahore Board, 2013)

(3) How does the equilibrium constant of a reaction tell us the direction of a chemical reaction (D.G. Khan Board, 2010; Rawalpindi Board, 2012) OR How the value of Kc of a reaction helps to predict the direction of a reversible reaction? (Sargodha Board, 2007; Gujranwala Board, 2014)

LE CHATLIER'S PRINCIPLE

Short Questions

(1) Give statement of (or Define) Le Chatlier's principle (D.G. Khan Board, 2007; Lahore Board, 2009, 2013; Azad Kashmir Board, 2012) OR Define law of mass action and Le-Chatlier's principle. (Rawalpindi Board, 2010) Ans: For Law of Mass Action, See page

(2) In some reversible reactions, the direction of reaction is changed by change in pressure. Give reason. (Bahawalpur Board, 2008)

(3) How does a catalyst affect a reversible reaction? (Faisalabad Board, 2008, 2010; Multan Board, 2008; Sargodha Board, 2013) OR Describe (or What is the) effect of catalyst on equilibrium. (Lahore Board, 2007; Bahawalpur Board, 2010; D.G. Khan Board, 2012; Faisalabad Board, 2012; Bahawalpur Board, 2012) OR A catalyst does not affect the equilibrium constant. Comment on it. (Gujranwala Board, 2008)

(4) What will be the effect on the position of equilibrium on the following system if: (a) temperature is increased, (b) chlorine is added (Lahore Board, 2010)

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad \Delta H = -90 \text{ kJ/mol}$$

Long Questions

(1) Define Le-Chatellier's principle. Discuss effect of (I) change in volume (II) change in temperature on the formation of ammonia. (D.G. Khan Board, 2012)

APPLICATIONS OF LE-CHATLIER'S PRINCIPLE

Short Questions

(1) How ammonia is synthesized by Haber's process. Also give the optimum conditions for reaction. (Sargodha Board, 2013)

(2) Formation of NH_3 is favoured at low temperature. Explain. (D.G. Khan Board, 2007) OR Why during the synthesis of NH_3 temperature is kept low? (Gujranwala Board, 2013)

(3) What will the effect of increase of pressure and temperature on the following reaction? (Gujranwala Board, 2013)

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) \qquad \Delta H = -92.46 \text{ kJ}$$ 2011)

(4) Increasing pressure increases the oxidation of SO_2 to SO_3. Explain why? (Bahawalpur Board)

(5) What will be the effect of volume change on the following system at equilibrium state? (Faisalabad Board, 2011)

(a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (b) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

Long Questions

(1) Write a note on synthesis of ammonia gas by Haber's process keeping in mind the applications of chemical equilibrium in industry. (Lahore Board, 2012)

IONIC PRODUCT OF WATER

Short Questions

(1) What is an ionic product of water? Give its value at room temperature. (Lahore Board, 2009) (Bahawalpur Board, 2010)
OR What is K_w. Give its value for water. (D.G. Khan Board, 2010)

(2) What is K_w? What is the effect of temperature on the value of K_w?

pH AND pOH

Short Questions

(1) Define pH and pOH (Gujranwala Board, 2008; Sargodha Board, 2010; D.G. Khan Board, 2012; Azad Kashmir Board, 2012; Multan Board, 2013; Lahore Board, 2013, 2014) OR Define pH with mathematical expression. (Sargodha Board, 2013)

(2) Prove that pH = -log of $[H^+]$ (Sargodha Board, 2007)

(3) What will be nature of solution when (Gujranwala Board, 2011)
(a) pH = 3.0, Ans: Since pH is less than 7, therefore, the solution is acidic
(b) pH = 8.0, Ans: Since pH is higher than 7, therefore, the solution is basic.

(4) What will be nature of solution when: (Gujranwala Board, 2012)
(a) pH is more than 7, Ans: Since pH is less than 7, therefore, the solution is acidic
(b) pH is smaller than 7, Ans: Since pH is higher than 7, therefore, the solution is basic

Long Questions

(1) Define pH and pOH. How are they related with pK_w (Bahawalpur Board, 2012)

IONIZATION CONSTANT OF AN ACID/BASE

Short Questions

(1) What are the factors affecting ionization of acids? (D.G. Khan Board, 2010)

(2) Define conjugate acid and base. (Multan Board, 2008)

(3) Prove $pK_a + pK_b = 14$ (Gujranwala Board, 2010)

(4) Prove that $pK_a + pK_b = pK_w$ (Faisalabad Board, 2012)

(5) What is pK_a and pK_b. (Lahore Board, 2014)

COMMON ION EFFECT

Short Questions

(1) Define common ion effect. Give two examples. (Faisalabad Board, 2010; Azad Kashmir Board, 2012; Lahore Board, 2014) OR What is common ion effect? (Gujranwala Board, 2010)

(2) How is NaCl purified by common ion effect? (Bahawalpur Board, 2009; Faisalabad Board, 2010; Sargodha Board, 2011) OR HCl is used in the purification of NaCl. Explain. (Multan Board, 2012)

(3) Why HCl is added before passing H_2S gas in qualitative analysis of 2nd group basic radicals. (Sargodha Board, 2013)

(4) Why solid NH_4Cl is added in qualitative analysis of 3rd group basic radicals before adding NH_4OH? (Faisalabad Board, 2013)

(5) Give two applications of common ion effect. (Gujranwala Board, 2012)

Long Questions

(1) State and explain the term common ion effect and give at least two examples. (Gujranwala Board, 2012; Azad Kashmir Board, 2012)

BUFFER SOLUTIONS, HANDERSON'S EQUATION, BUFFER CAPACITY

Short Questions

(1) What are buffer solutions? How are they prepared? (Bahawalpur Board, 2008) OR What is buffer solution? Give examples (D.G. Khan Board, 2009; Bahawalpur Board, 2012)

(2) What are buffer solutions? Why do we need buffer solutions? (Multan Board, 2007; Faisalabad Board, 2007; D.G. Khan Board, 2008; Sargodha Board, 2012; Gujranwala Board, 2012) OR Buffers are

(3) Important in many areas of chemistry. Justify it. (Sargodha Board, 2013)

(4) What are buffer solutions? How an acidic buffer is prepared? (Gujranwala Board, 2011; Sargodha Board, 2011; Multan Board, 2013)

(5) What are basic buffer solutions? (Lahore Board, 2008)

(6) How does the buffer act? (Faisalabad Board, 2010; Multan Board, 2010)

(7) What are buffer solutions? Write two uses (or applications) of buffer solutions (Lahore Board, 2011, 2013; D.G. Khan Board, 2012; Faisalabad Board, 2013)

(8) What is Henderson equation? (Faisalabad Board, 2008; Multan Board, 2012; Lahore Board, 2014)

(9) Represent Hendersons equation for acidic and basic buffer solutions. (Multan Board, 2009; Sargodha Board, 2011)

(10) Write Henderson's equation for acidic buffer. (Rawalpindi Board, 2007; Bahawalpur Board, 2010, 2011)

(1) What is (or Define) buffer capacity? (Multan Board, 2008; Rawalpindi Board, 2009) (Faisalabad Board, 2012) OR Explain the terms buffer and buffer capacity. (Sargodha Board, 2012) OR Define with examples (i) Buffer, (ii) Buffer capacity (Bahawalpur Board, 2011; Multan Board, 2012)

Long Questions

(1) Derive the "HENDERSON'S EQUATION" for acidic buffer. (D.G. Khan Board, 2012)

SOLUBILITY PRODUCT

Short Questions

(1) Define buffer capacity and solubility product (Bahawalpur Board, 2009) OR Define solubility and solubility product and common ion effect (Rawalpindi Board, 2010) OR Define solubility product. (Rawalpindi Board, 2011)

(2) What is meant by solubility product constant? (Multan Board, 2010) OR Define solubility product with examples. (Gujranwala Board, 2013)

(3) Give the two applications of the solubility product. (Multan Board, 2011; Rawalpindi Board, 2012; Lahore Board, 2013) OR Define solubility product. Give its applications. (D.G. Khan Board, 2011; Gujranwala Board, 2014)

(4) What is the effect of presence of common ion on solubility? Give example. (Lahore Board, 2009; Sargodha Board, 2009; Sargodha Board, 2010; Faisalabad Board, 2012; Multan Board, 2012, 2013)

TEST YOUR SKILLS

Marks: 85

OBJECTIVE

Time: 20 Minutes Marks: 17

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) In an endothermic reversible reaction, increase in temperature shifts the equilibrium to
(a) Reactant side (b) Product side (c) Remains unchanged (d) None

(ii) By adding NH_4Cl to NH_4OH solution, the ionization of NH_4OH
(a) Increases (b) Decreases (c) Remains same (d) Increases 100 times

(iii) Solubility of KI is endothermic. Its solubility is increased
(a) at high temperature (b) at low temperature (c) independent of temperature (d) at moderate temperature

(iv) When a catalyst is added to a system in equilibrium, the equilibrium concentration of reactant
(a) Decrease (b) Increase (c) Remains constant (d) Sharply increases

(v) PH of tomato is
(a) 1.2 (b) 4.2 (c) 7.2 (d) 9.2

(vi) When K_c value is small the equilibrium position is
(a) towards left (b) towards right (c) remains unchanged (d) none of these

(vii) The equilibrium constant K_c can be expressed in units of
(a) mol dm^{-3} (b) g dm^{-3} (c) depends upon reaction (d) dimensionless

(viii) Purification of rock salt by passing HCl gas is due to
(a) ionization effect (b) common ion effect (c) solubility effect (d) catalytic effect

(ix) A basic buffer solution can be prepared by mixing
(a) strong acid and its salt with weak base (b) weak base and its salt with strong acid
(c) strong base and its salt with weak acid (d) weak acid and its salt with strong base

(x) In Haber Process, for formation of NH_3 the pressure used is
(a) 100 atm (b) 200-300 atm (c) 600 atm (d) 1000 atm

(xi) Which one of the following reaction has no units of its Kc value.
(a) $2SO_2 + O_2 \rightleftharpoons 2SO_3$ (b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(c) $2HI \rightleftharpoons H_2 + I_2$ (d) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

(xii) The relationship Kp and Kc for a gaseous reaction is $Kp = Kc(RT)^{\Delta n}$ The value of Kp and Kc are same when
(a) reaction occurs at STP (b) reaction is exothermic
(c) reaction is endothermic (d) number of moles of products and reactants are same.

(xiii) The ionic product of H^+ ions and OH^- in water is called ionization constant of water Kw. The value of Kw at 25° is
(a) 0.11×10^{-14} (b) 0.30×10^{-14} (c) 1.0×10^{-14} (d) 3.00×10^{-14}

(xiv) Reaction of BiCl3 with H2O gives white ppt. of BiOCl and HCl is formed. The white ppt. disappears by
(a) adding $BiCl_3$ (b) adding HCl (c) increasing temperature (d) decreasing temperature

(xv) If the difference of pKa values of the two acids is 2, then
(a) acid with smaller pKa is 10 times stronger acid. (b) acid with greater pKa is 10 times stronger acid.
(c) acid with smaller pKa is 100 times stronger acid. (d) acid with greater pKa is 100 times stronger acid

(xvi) Which one of the following is a buffer?
(a) HCl + NaCl solution (b) $CH_3COOH + CH_3COONH_4$ solution
(c) $H_2CO_3 + CaSO_4$ solution (d) $CH_3COOH + CH_3COONa$

(xvii) A certain solution has $P^H = 5$. Its OH^- ion concentration in mole dm^{-3} is
(a) 1.0×10^{-9} (b) 1.0×10^{-5} (c) 1.0×10^{-14} (d) 1×10^{0}

SUBJECTIVE

Time 2:10 Hours Marks: 68

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question numbers carefully. (22x 2)=44

Section - I

Q2. Answer any Eight parts from the followings.

(i) What is the effect of changing temperature on an equilibrium system?

(ii) Derive equilibrium constant expressions for the dissociation of PCl_5

(iii) Prove that $1dm^3$ of H_2O contain 10^{-7} moles of H^+ ions at 25°C.

(iv) What is the relationship between K_p and K_c for a reversible reaction?

(v) Some gaseous reaction are not affected by pressure changes. Why?

(vi) Formation of NH_3 from 'N_2' and 'H_2' is favoured at low temperature. Explain it?

(vii) Ionic product of water increase with increase in temperature. Why?

(viii) How NaCl can be purified by common ion effect?

(ix) Why buffers are important?

(x) When concentration of a salt is increased in an acidic buffer, then the pH of solution increases. Why

(xi) What is the effect of common ion on solubility of salts?

(xii) Derive Ksp expression for solubility of $PbCl_2$.

Q3. Answer any Eight parts from the followings.

(i) The change of temperature disturbs both the equilibrium position and equilibrium constant of reaction. Explain with reason?

(ii) What is equilibrium constant K_c?

(iii) For what type of reactions K_c and K_p are equal. Give example?

(iv) What are conjugate acid base pair?

(v) What happens if the concentration ratio $\frac{[products]}{[reactants]} \neq Kc$?

(vi) Increasing pressure increases the conversion of SO_2 to SO_3. Why ?

(vii) How temperature affects a reversible reaction?

(viii) Why decrease in temperature favours exothermic reactions?

(ix) Define pH and pOH?

(x) What is the effect of catalyst on a system at equilibrium?

(xi) What are the optimum conditions to get maximum yield of NH_3?

(xii) What is K_w? How is it affected by temperature?

Q4. Answer any Six parts from the followings.

(i) Show that water is a weak electrolyte?

(ii) What is the nature of a solution having pH=9. What is its effect on litmus paper?

(iii) If $K_a K_b = K_w$, then what is the value of pKa + pKb at 25°C?

(iv) What are buffer solutions? How an acidic buffer is prepared?

(v) pKa of a certain acid A is -7, while that of an acid B is -5. Which acid is stronger and how much?

(vi) What happens if acid is added to the $CH_3COOH + CH_3COONa$ buffer?

(vii) The pH of buffer of $CH_3COOH + CH_3COONa$ is 3.76, then what is the concentration of acetic acid, if $[CH_3COOH] = 1.0$ mol/dm^3?

(viii) Define pH and p OH?

(ix) What is the effect of a common ion on the solubility?

Section - II (Attempt any three questions) (8x 3)=24

Q3. (a) Derive Handerson's equation for acidic buffer. (04)
(b) What is Le-Chatlier's principle? Discuss effect of concentration on an equilibrium system. (04)

Q4. (a) How does a buffer work? (02)
(b) Discuss optimum conditions required for the synthesis of SO_3 (04)
(c) Differentiate between reversible and irreversible processes. (02)

Q5. (a) How does K_c help to predict the direction of reaction? (02)
(b) What is law of mass action? Derive an equation for Kc expression of a general reversible reaction. (05)
(c) Benzoic acid C_6H_5COOH is a weak mono-basic acid ($Ka = 6.4 \times 10^{-5}$ mol/dm^3). What is the pH of a solution containing 7.2 g of sodium benzoate in one dm^3 of 0.02 mol/dm^3 benzoic acid. (03)

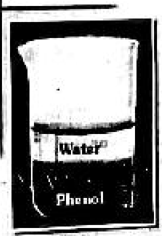
Q6. (a) What is the percentage ionization of acetic acid in a solution in which 0.1 moles of it has been dissolved per dm^3 of the solution, $Ka = 1.85 \times 10^{-5}$. (03)
(b) What is buffer action? (02)
(c) Prove that $K_a K_b = K_w$ (03)

Q7. (a) What are the effects of changing temperature pressure and concentration on the following gaseous reactions? (04)
(i) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ (ii) $2HI \rightleftharpoons H_2 + I_2$
(b) The solubility of CaF_2 in water at 25°C is found to be 2.05×10^{-4} mol/dm^3 what is the value of Ksp at this temperature. (04)

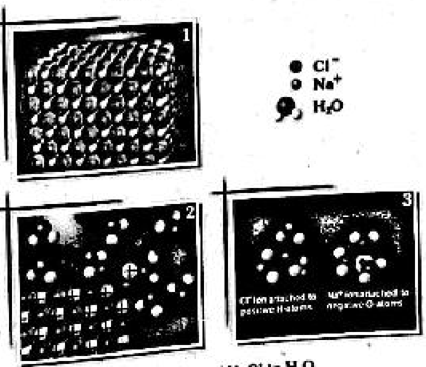
Things to Remember

Chapter 9

SOLUTIONS



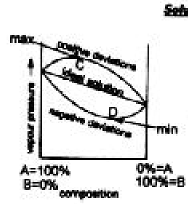
Phenol Water system



Dissolution of NaCl in H_2O

CONTENTS

Chapter-9 Solutions



CONCEPT OF A SOLUTION

Phase

A sample of matter with uniform properties and fixed composition is called a Phase.

Example

- Water at normal temperature and pressure is a single phase
- A solution of sugar in water is also a single phase

Solution

A homogenous mixture of two or more substances is called a solution.

Example

Solution of sugar in water.

Binary Solution

A solution composed of two substances is called binary solution.

Example

Solution of NaCl in H_2O

Solvent

A substance present in larger amount in a solution is called solvent.

Solute

A substance present in smaller amount in a solution is called solute.

Example

In 10% sugar solution, sugar is solute while H_2O is solvent.

Dilute Solution

A solution containing relatively small amount of solute dissolved in a solvent is called dilute solution.

Concentrated Solution

A solution containing relatively larger amount of solute dissolved in a solvent is called concentrated solution.

Example

A 10% sugar solution is more concentrated than 5% sugar solution.

Aqueous Solution

A solution in which water is solvent is called aqueous solution.

Example

Solution of NaCl in H_2O

Concentration of Solution

The amount of solute present in a given amount of solvent is called concentration of solution.

Exercise Q5 (a): *What are the concentration units of solutions. Compare molar and molal solutions.* ***(For Comparison see below molality on page 507)***

CONCENTRATION UNITS OF SOLUTION

Units used to express the amount of solute in solution are called concentration units of solution.

Following concentration units are generally used.

1. Percentage composition 2. Molarity 3. Molality 4. Mole fraction 5. Parts per million

Percentage Composition

It can be expressed in following ways

i) __Percentage Weight/Weight (% w/w)__

It is the weight of solute dissolved per 100 parts by weight of solution.

Mathematically

$$\%\text{ by weight} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

__Example__

A 5% (w/w) sugar solution in water means that 5 g. of solute are present in 100 g of solution in water. This solution contains 95 g of water.

Example 1

Calculate the percentage by weight of NaCl, if 2 g of NaCl is dissolved in 20 g of water.

__**Solution**__

Mass of NaCl = 2 g

Mass of H_2O = 20 g

Mass of Solution = 20 + 2 = 22 g

$$\%\text{ by weight of NaCl} = \frac{\text{mass of NaCl}}{\text{mass of solution}} \times 100$$

$$\%\text{ by weight of NaCl} = \frac{2}{22} \times 100 = \boxed{9.09\%}$$

ii) __Percentage weight/volume (% w/v)__

It is the weight of solute dissolved per 100 parts by volume of solution.

__Example__

A 10% (w/v) glucose solution in water means that 10 g of glucose are present in 100 cm^3 of solution.

In this solution, quantity of solvent is not known exactly.

iii) __Percentage volume/weight (% v/w)__

It is the number of cm^3 of solute dissolved per 100 g of solution.

__Example__

A 10% (v/w) solution of alcohol in water means that 10 cm^3 of alcohol are present in 100 g of solution.

In this solution, total volume of solution is not known exactly.

iv) __Percentage volume/volume (% v/v)__

It is the volume of solute dissolved per 100 cm^3 of solution.

This unit is used for solutions of liquids in liquids.

__Example__

A 12% solution of alcohol in water means that 12 cm^3 of alcohol are present in 100 cm^3 of solution.

__For such solutions, total volume of solution may not be equal to the sum of volumes of solute and solvent.__

Molarity (M)

Number of moles of solute dissolved in 1 dm^3 of solution is called molarity.

It is denoted by 'M'

Mathematically

$$M = \frac{\text{Number of moles of solute}}{\text{Volume of solution in } dm^3}$$

Since $\quad \text{Number of moles} = \dfrac{\text{Mass of solute}}{\text{Molecular mass of solute}}$

Thus $\quad M = \dfrac{\text{Mass of solute}}{\text{Molecular mass of solute}} \times \dfrac{1}{\text{Volume of solution in } dm^3}$

__Example__

- 180 g (1 mole) of glucose are dissolved in H_2O and volume of solution is made up to 1 dm^3 by adding more H_2O to prepare 1M solution.

- 342 g (1 mole) of sucrose are dissolved in water and volume is made up to 1 dm^3 by adding more H_2O to prepare 1M solution.

Similarly

- Since 342 g of sucrose have larger volume than 180 g of glucose, therefore, in 1 molar sucrose solution, amount of H_2O is less than 1 molar glucose solution.
- Exact volume of solvent can be determined by noting its density.

Example 2:
Calculate the molarity of a solution containing 20.7 g of K_2CO_3 dissolved in 500 cm^3 of the given solution.

Solution:

Mass of K_2CO_3 $= w = 20.7\ g$
Molar mass of K_2CO_3 $= M = 138\ g/mol$
Volume of solution $= V = 500\ cm^3 = \frac{500}{1000} = 0.5\ dm^3$
Molarity $= ?$

Molarity is given by

$$\text{molarity} = \frac{w}{M} \times \frac{1}{V}$$

$$\text{molarity} = \frac{20.7}{138} \times \frac{1}{0.5} = \boxed{0.3\ mol/dm^3}\ \boxed{\text{or } 0.3\ M}$$

Molality (m)

Number of moles of solute dissolved in 1 kg. of solvent is called molality.

It is denoted by 'm'

Mathematically

$$m = \frac{\text{Number of moles of solute}}{\text{Mass of solvent in Kg}}$$

Since $\text{Number of moles} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute}}$

Thus $m = \frac{\text{Mass of solute}}{\text{Molecular Mass of solute}} \times \frac{1}{\text{Mass of solvent in Kg}}$

Examples

- 180 g of glucose when dissolved in 1 kg (1000g) of water gives 1 molal solution of glucose. Total mass of this solution is 1180 g. However, total volume of this solution is not known exactly. To find the total volume, density of solution is required.

- For 1 molal sucrose solution, 342g of sucrose are dissolved in 1000 g of H_2O
- Molality of a solution is an indirect expression of the ratio of moles of solute to solvent.

Comparison of Molar and Molal Solutions

- 1 molal aqueous solution of any substance is dilute than its 1 molar solution. Since in 1 molal solution quantity of solvent is greater.
- The value of molality does not change with temperature but molarity changes. It is because molar solutions are based upon volume, which changes with temperature, hence molarity changes. But molal solutions are based upon mass which is not changed with temperature.

Example 3
What is the molality of a solution prepared by dissolving 5 g of toluene (C_7H_8) in 250 g of benzene. (Bahawalpur Board, 2011)

Solution

Mass of toluene(solute) $= w = 5\ g$
Molar mass of C_7H_8 $= M = 92\ g/mol$
Mass of benzene (solvent) $= W = 250\ g = 0.250\ kg$
Molality $= ?$

Molality is given by

$$\text{Molality} = \frac{w}{M} \times \frac{1}{W}$$

$$\text{Molality} = \frac{5}{92} \times \frac{1}{0.250} = \boxed{0.217\ mol/kg} \text{ or } \boxed{0.217\ m}$$

Mole Fraction (x)

It is the ratio of the number of moles of a particular component of the solution to the total number of moles of all the components of the solution.

It is represented by 'x'

Mathematically

$$x = \frac{\text{Number of moles of one compponent}}{\text{Total number of moles of all components of solution}}$$

This unit is also applicable to a solution having more than two components. e.g. consider three components A, B and C in a solution. Let number of moles of A, B and C are n_A, n_B and n_C respectively. The mole fractions of of these components in the solution are given by

$$X_A = \frac{n_A}{n_A + n_B + n_C} \quad , \quad X_B = \frac{n_B}{n_A + n_B + n_C} \quad , \quad X_C = \frac{n_C}{n_A + n_B + n_C}$$

- In a given solution, the sum of mole fractions of all components is always unity.
  e.g. in the above example
  $X_1 + X_2 + X_3 = 1$
- Mole fraction has no unit
- Mole pecentage can be obtained by multiplying mole fraction by 100.
  i.e. Mole percentage = Mole fraction × 100

Example 4
Calculate the mole fraction and mole percent of each component in a solution having 92 g of ethyl alcohol, 96 g of methyl alcohol and 90 g of water.

Solution

Mass of ethyl alcohol = 92 g
Molar mass of ethyl alcohol = 46 g

$$\text{Moles of ethyl alcohol} = \frac{92}{46} = 2 \text{ moles}$$

Mass of methyl alcohol = 96 g
Molar mass of methyl alcohol = 32 g

$$\text{Moles of methyl alcohol} = \frac{96}{32} = 3 \text{ moles}$$

Mass of water = 90 g
Molar mass of water = 18 g

$$\text{Moles of water} = \frac{90}{18} = 5 \text{ moles}$$

Mole fractions are given by

$$X_{ethyl\ alcohol} = \frac{2}{2+3+5} = 0.2$$

$$X_{methyl\ alcohol} = \frac{3}{2+3+5} = 0.3$$

$$X_{water} = \frac{5}{2+3+5} = 0.5$$

Mole percents are given by
Mole percent of ethyl alcohol = 0.2 × 100 = $\boxed{20\ \%}$
Mole percent of methyl alcohol = 0.3 × 100 = $\boxed{30\ \%}$
Mole percent of water = 0.5 × 100 = $\boxed{50\ \%}$

Parts Per Million (ppm)

It is the number of parts of solute (by weight or volume) present per million parts (by weight or volume) of solution.

Mathematically

$$\text{ppm} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

This unit is used to express very low concentrations. e.g. to express the conc. of impurities in water.

Example 5
Sea water has 5.65 × 10⁻³ g of dissolved oxygen in one kg of water. Calculate the concentration of oxygen in sea water in ppm.

Solution:

Mass of oxygen = 5.65×10^{-3} g
Mass of water = 1 kg = 1000 g
ppm of oxygen = ?

ppm is given by

$$\text{ppm} = \frac{5.65 \times 10^{-3}}{1000} \times 10^6 = \boxed{5.65\ \text{ppm}}$$

Interconversion of Various Concentration Units of Solutions

Various concentration units can be converted into one another. Sometimes chemical suppliers provide solution whose molarity is given. If we want to know its molality or w/w percentage then we need to convert one unit into other. These conversions are usually done by using formula masses and densities of solutes or solutions.

Name of acid	% (w/w)	Molarity (M dm^{-3})	Density (g cm^{-3})
H_2SO_4	98 %	18	1.84
H_3PO_4	85.5 %	4.8	1.70
HNO_3	70.4 %	15.9	1.42
HCl	37.2 %	12.1	1.19
CH_3COOH	99.8 %	17.4	1.06

Example 6

Calculate the molality of 8% (w/w) of NaCl solution.

Solution

8% (w/w) of NaCl solution mean 8 g of NaCl are dissolved in 100 g of solution

Therefore

Mass of NaCl (solute) = w = 8 g

Mass of H_2O (solvent) = W = 100 − 8 = 92 g = $\frac{92}{1000}$ = 0.092 kg

Formula mass of NaCl = M = 58.5 g/mol

Molarity is given by

$$\text{Molality} = \frac{w}{M} \times \frac{1}{W}$$

$$\text{Molality} = \frac{8}{58.5} \times \frac{1}{0.092} = \boxed{1.487\ \text{mol/kg}} \text{ or } \boxed{1.487\text{m}}$$

Example 7

Hydrochloric acid available in lab is 36% (w/w) . The density of HCl solution is 1.19 g/cm³. Determine the molarity of HCl solution.

Solution

36% (w/w) HCl solution means that 36 g of HCl are present in 100 g of solution

Mass of HCl = 36 g
Mass of solution = 100 g
Density of solution = 1.19 g/cm³
Molarity = ?

Now

1 cm³ of solution weighs = 1.19 g
1000 cm³ of solution weighs = 1.19 × 1000 = 1190 g.

Since

100 g of HCl solution contain pure HCl = 36 g

1190 g of HCl solution contain pure HCl = $\frac{36 \times 1190}{100}$ = 428.4 g

Thus 1000 cm³ of solution contain HCl = 428.4 g

Hence

Mass of HCl = w = 428.4 g
Molar Mass of HCl = M = 36.5 g
Volume = V = 1000 cm³ = 1 dm³

Molarity is given by

$$\text{molarity} = \frac{w}{M} \times \frac{1}{V}$$

$$\text{molarity} = \frac{428.4}{36.5} \times \frac{1}{1} = \boxed{11.73\ \text{mol/dm}^3} \text{ or } \boxed{11.73\ \text{M}}$$

Example 8

9.2 molar $HClO_4$ is available from the market. The density of the acid solution is 1.54 g/cm³. What is the percentage by weight of $HClO_4$.

Solution

1 cm³ of $HClO_4$ weighs = 1.54 g
1000 cm³ of $HClO_4$ weighs = 1.54 × 1000 = 1540 g.

Molarity of $HClO_4$ solution = 9.2 M
Molar Mass of $HClO_4$ = 100.5 g
Amount of $HClO_4$ / dm³ = Molarity × Mol. Mass
= 9.2 × 100.5 = 924.6 g

Hence

Total mass of solution = 1540 g
Mass of $HClO_4$ = 924.6 g
Mass of H_2O = 1540 − 924.6 = 615.4 g

Thus % by weights are given by

$$\%\text{ by weight of } HClO_4 = \frac{924.6}{1540} \times 100 = \boxed{60.04\%}$$

$$\%\text{ by weight of } H_2O = \frac{615.4}{1540} \times 100 = \boxed{39.96\%}$$

TYPES OF SOLUTIONS

Most common type of solution is solid in liquid. e.g. NaCl in water. However, many other types of solutions are also present.

There are three common states of matter

i) Gas
ii) Liquid
iii) Solid

Therefore, there are nine possible types of solution

Table: Common types and examples of solution

Sr. No	Solute State	Solvent State	Examples
1.	Gas	Gas	Air
2.	Gas	Liquid	O_2 in water, CO_2 in water
3.	Gas	Solid	H_2 adsorbed by Pd
4.	Liquid	Gas	Mist, Fog, Clouds, Liquid air pollutants
5.	Liquid	Liquid	Alcohol in water, milk, benzene in toluene
6.	Liquid	Solid	Mercury in silver, butter, cheese
7.	Solid	Gas	Dust particles in smoke
8.	Solid	Liquid	Sugar in water, Jellies, Paints
9.	Solid	Solid	Metal alloys, Pearls, opals, carbon in steel

Solution of solids in liquids

Dissolution

The solubility of a solid substance in liquid is called dissolution

The process of dissolution depends upon forces between solute and solvent.

Example

Dissolution of NaCl in H_2O

Solubility Principle

Solubility principle states

" Like dissolves Like "

i.e. Polar substances are dissolved in polar solvents and

Non-polar substances are dissolved in non-polar solvents.

Explanation

In solids, ions or molecules are tightly packed and have strong intermolecular or inter-ionic forces. The process of dissolution is to break these forces. These forces are broken up by solute-solvent interactions and thus solid is dissolved in the solvent.

In ionic solids, strong interionic forces are present.

For dissolution, these forces must be broken. Only polar solvents with strong attractive forces can break these forces. Hence, ionic solids are mostly dissolved in polar solvents.

In non-polar molecular crystals, weak London or dipole-dipole forces are present. These can be broken easily by non-polar solvents. Hence, non-polar solids are dissolved in non-polar solvents.

Examples

- Cane-sugar with strong hydrogen bonding is polar. It does not dissolve in non-polar solvents such as kerosine oil, petrol, benzene etc. because these solvents can not break H-bonding of cane-sugar.

  But it readily dissolve in H_2O because they develop H-bonding for each other.
- NaCl with strong interionic forces in not dissolved in moderately polar solvent such as acetone. But at once dissolved in polar H_2O.

Solution of Liquids in Liquids

It may be divided into three types

i. Completely miscible liquids

Liquids which dissolve together in all proportion are called completely miscible liquids.

Example

Solution of alcohol in H_2O

- During formation of such solution volume is decreased or in some cases increases
- Heat may be evolved or absorbed during their formation
- These solution can be separated by fractional distillation

ii. Partially miscible liquids

The liquids which dissolve together to some extent are called partially miscible liquids

In ether-water system, ether (C_2H_5-O-C_2H_5) dissolves water upto 1.2% while water dissolves ether upto 6.5%.

Thus if equal volume of ether and water are shaken together, two layers are produced.

- Water containing ether and
- Ether containing water

Each layer is a saturated solution of other liquid

Conjugate Solutions

When two liquids are mixed together such that two layers are produced and each layer is a saturated solution of other liquid then such solutions are called conjugate solutions

Mutual solubility of liquids in conjugate solutions changes with temperature.

Examples

- Phenol-Water system
- Triethylamine – water system
- Nicotine – water system

Exercise Q9 (b)
Explain the effect of temperature on phenol-water system.

Phenol-Water system

By shaking equal volume of phenol and water together, two layers are produced.

- Upper layer of water containing phenol, and
- Lower layer of phenol containing water.

At 25°C upper layer is 5% solution of phenol in water, while

lower layer is 30% solution of water in phenol.

In upper layer phenol is solute while in lower layer water is solute.

These two solutions (layers) are called conjugate solution.

The lower layer has greater density due to greater percentage of phenol.

When temperature is increased, more water moves into phenol and more phenol move into water. At 65.9°C a homogenous mixture of phenol and water is obtained. This mixture contains 34% phenol and 66% water. 65.9°C is called upper consulate temperature or critical solution temperature of this system.

Consulate Temperature

The temperature at which two conjugate solutions merge into each other to form homogenous mixture is called critical solution temperature or consulate temperature.

Different systems have their own consulate temperature and composition.

Examples

Water–Aniline system has upper consulate temperature of 167 °C with 15% H_2O

Methanol–cyclohexane system has upper consulate temperature of 49.1°C with 29% methanol.

(iii) Completely immiscible liquids

The liquids, which do not dissolve into each other in any proportion, are called completely immiscible liquids.

Examples

Water - Benzene ($H_2O + C_6H_6$)

CS_2 - Water ($H_2O + CS_2$)

Exercise Q13. *What is Raoult's law. Give its three statements. How this law can help us to understand the ideality of a solution.*

RAOULT'S LAW

It was given by F.M. Raoult in 1887

It states

The vapour pressure of a solvent above a solution, is equal to the product of the vapour pressure of pure solvent and mole fraction of solvent in solution.

Mathematically

$$P = P^o x_1 \quad \_\_\_ (1)$$

Where

P = Vapour pressure of solvent in solution

P^o = Vapour pressure of pure solvent.

x_1 = Mole fraction of solvent

Since

$x_1 + x_2 = 1$

Where x_2 = mole fraction of solute

Then

$$x_1 = 1 - x_2 \quad \_\_\_ (2)$$

Put the value of x_1 from eq (2) in eq (1)

$$P = P^o (1 - x_2)$$

or

$$P = P^o - P^o x_2$$

$$P^o - P = P^o x_2$$

$$\Delta P = P^o x_2 \quad \_\_\_ (3)$$

Where ΔP = Lowering of Vapour pressure

or

$$\Delta P \propto x_2$$

Thus, Raoults law can also be stated as

Lowering of vapour pressure of a solution, is directly proportional to the mole fraction of solute.

or Mathematically $\Delta P \propto x_2$

From eq (3) we have

$$\frac{\Delta P}{P^o} = x_2$$

Where $\frac{\Delta P}{P^0}$ = Relative lowering of vapour pressure

Thus

Relative lowering of vapour pressure of a solution is equal to the mole fraction of solute

Facts about relative lowering of Vapour Pressure

- It is independent of the temperature
- It depends upon the conc. of solute
- It is same when equimolar amounts of different solutes are dissolved in the same amount of the same solvent.

Raoult's Law and Ideality of solutions

A solution, which obeys Raoult's law, is called an ideal solution. Thus, Raoult's law can help to distinguish the ideal and non-ideal behaviour of solutions.

Example 9

The vapour pressure of water at 30°C is 28.4 torr. Calculate the vapour pressure of a solution containing 70 g of cane sugar ($C_{12}H_{22}O_{11}$) in 1000 g of water at the same temperature. Also calculate the lowering of vapour pressure.

Solution

Mass of Cane Sugar = 70 g

Molar Mass of Cane sugar ($C_{12}H_{22}O_{11}$) = 342 g

Moles of cane sugar $= n_2 = \frac{70}{342} = 0.20$ moles

Mass of water = 1000 g

Molar Mass of water = 18 g

Moles of water $= n_1 = \frac{1000}{18} = 55.5$ moles

Thus Mole fraction of cane sugar $= x_2 = \frac{0.2}{0.20 + 55.5} = 0.0036$

Mole fraction of water $= x_1 = \frac{55.5}{0.20 + 55.5} = 0.9964$

Hence

Mole fraction of water $= x_1 = 0.9964$

Vapour pressure of pure water $= P^0 = 28.4$ torr

Vapour pressure of solution $= P = ?$

According to Raoult's law

$P = P^0 x_1 = 28.4 \times 0.9964 = 28.29$ torr

So lowering of vapour pressure $= 28.4 - 28.29 = \boxed{0.11 \text{ torr}}$

Raoult's Law for two Volatile Components

In a solution of two volatile components A and B, the vapour pressure of each component above the solution is proportional to its mole fraction in the solution.

i.e. For liquid A For liquid B

$P_A = P^0_A\, x_A$ $P_B = P^0_B\, x_B$

Where P_A = Vapour pressure of A above solution

P_B = Vapour pressure of B above solution

P^0_A = Vapour pressure of pure A

P^0_B = Vapour pressure of pure B

x_A = Mole fraction of A

x_B = Mole fraction of B

According to Dalton's law, total pressure of the solution is equal to the sum of individual pressures of A and B.

i.e. $P_t = P_A + P_B$

or $P_t = P^0_A x_A + P^0_B x_B$

Since $x_A + x_B = 1$ or $x_A = 1 - x_B$

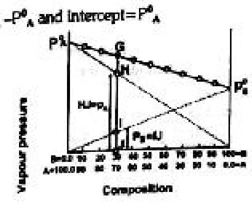
Hence $P_t = P^0_A (1 - x_B) + P^0_B x_B$

$P_t = P^0_A - P^0_A x_B + P^0_B x_B$

$P_t = (P^0_B - P^0_A) x_B + P^0_A$

This is an equation of straight line with slope $= P^0_B - P^0_A$ and intercept $= P^0_A$

Only ideal solutions will give straight lines.



Graph shows following things

- Dotted lines represent the vapour pressure of each component in the solution, which increases with increase in mole fraction.
- The vapour pressure of solution is given by the straight line joining P^0_A and P^0_B.

- Vapour pressure of solution is never greater than P^{o}_{A} or less than P^{o}_{B}.
  i.e. it remains intermediate between P^{o}_{A} and P^{o}_{B}.
- Vapour pressure of each component in the solution is always less than its vapour pressure in pure form.
- Total Pressure of solution is equal to the sum of individual pressures of components A and B in the solution.

  e.g. consider the point G in the fig. At this point vapour pressure of A is P_A (HJ) and that of B is P_B (IJ). Thus, total vapour pressure of solution at G will be $P_t = P_A + P_B = HJ + IJ$

IDEAL AND NON-IDEAL SOLUTIONS

Ideal Solutions

(1) ***A solution, which obeys Raoult's law, is called an ideal solution.***

(2) During formation of an ideal solution, heat is not evolved or absorbed. i.e., enthalpy change is zero, $\Delta H = 0$.

(3) Total volume of solution is equal to the sum of volume of components of solution.

(4) Forces of attraction among molecules of components remain same in the solution just as they were in pure form.

Examples

Benzene – Toluene, Benzene – Ether, Chlorobenzene–Bromobenzene, Ethyl iodide – Ethyl bromide etc.

Non Ideal Solutions

(1) ***A solution which does not obey Raoult's law is called a non-ideal solution.***

(2) During formation of a non-ideal solution, heat may evolve or absorb. i.e., enthalpy change is not zero $\Delta H \neq 0$

(3) Total volume of solution is not equal to the sum of volume of components of solution.

(4) Forces of attraction among molecules of components do not remain same in the solution just as they were in pure form.

Examples:

Ethanol-Water, HCl-Water etc.

Difference between Ideal and Non-Ideal solutions.

	Ideal Solutions		Non ideal Solutions
1	A solution, which obeys Raoult's law, is called an ideal solution.	1	A solution which does not obey Raoult's law is called a non-ideal solution.
2	During formation of an ideal solution, heat is not evolved or absorbed. i.e., enthalpy change is zero ($\Delta H=0$)	2	During formation of a non-ideal solution, heat may evolve or absorb. i.e., enthalpy change is not zero ($\Delta H \neq 0$)
3	Total volume of solution is equal to the sum of volume of components of solution.	3	Total volume of solution is not equal to the sum of volume of components of solution.
4	Forces of attraction among molecules of components do not remain same in the solution just as they were in pure form.	4	Forces of attraction among molecules of components do not remain same in the solution just as they were in pure form.
5	Examples Benzene – Toluene, Benzene – Ether, Ethyl iodide – Ethyl bromide etc.	5	*Examples:* Ethanol-Water, HCl-Water etc.

VAPOUR PRESSURE OF LIQUID-LIQUID SOLUTIONS

Exercise Q8. (a):

Explain fractional distillation. Justify the two curves when composition is plotted against boiling point of solutions.

Ideal Solution

A solution which obeys Raoult's law is called an ideal solution.

Fractional Distillation

The separation of liquids from a liquid mixture on the basis of their boiling point is called Fractional distillation.

Fractional Distillation of Ideal Solution

Consider a solution of two volatile components A and B. Let A is more volatile than B, hence A has lower boiling point than B

Let solutions of various compositions are made and composition of solution and its vapours is plotted on X-axis against their boiling temperature on Y-axis.

Thus, two curves are obtained as shown in the fig

- Lower curve gives the composition of solution at different temperature, while
- Upper curve gives the composition of vapours in equilibrium with solution at different temperature.

Two curves are obtained because vapours and solution have different composition at different temperature.

When such liquid mixture is heated to point G, then

- Composition of solution is given by C which have more B and less A, while
- Composition of vapours is given by D which have more A and less B.

Since A is more volatile, therefore at each temperature, vapours have more % of A than B. ***The liquid mixture left behind is called residue and the vapours obtained are called distillate.***

The distillate obtained is cooled and again distilled. The re-distilled vapours will become richer in A than before and if this process is repeated many times then vapours will go on richer in A and residue will go on richer in B. Hence both A and B can be separated. A will pass over while B will be left behind. Such a mixture is called zeotropic mixture.

Zeotropic Mixtures

Liquids which distile with change in composition are called zeotropic mixtures.

Zeotropic mixture can be easily separated into their components.

Example:

Methyl alcohol – water solution can be separated by distillation.

Exercise Q7.

What are non-ideal solutions? Discuss their types and give three example of each.

Exercise Q 8(b)

The solutions showing positive and negative deviations cannot be fractionally distilled at their specific compositions. Explain it.

Exercise Q9.(a)

What are azeotropic mixtures? Explain them with the help of graphs?

Non-Ideal Solutions (Azeotropic Mixtures)

A solution, which does not obey Raoult's law, is called a non-ideal solution.

They show deviations due to difference in their molecular structure i.e. size, shape and intermolecular forces.

Azeotropic Mixtures

The liquid mixtures, which boil at constant temperature and distil over without change in composition like a pure compound, at any temperature are called azeotropic mixtures.

These are not true chemical compounds. Because their composition can be changed by changing conditions such as pressure. While composition of pure chemical compound remains constant at different temperature and pressure.

Fractional distillation of Non-Ideal Solutions

Non-ideal solutions show either maximum or minimum in their vapour pressure curve. Hence, they cannot be separated completely by fractional distillation.

Non-ideal solutions show two types of deviations

- Positive deviations
- Negative deviations

Vapour pressure–composition diagram for both types is shown in the fig.

Positive Deviations (Minimum Boiling Azeotrope)

Liquid solutions which have maximum in their vapour pressure curve shows positive deviations from Raoult's law.

Consider a solution of two components A and B, in which A is more volatile than B. In fig, at point C, vapour pressure of solution is maximum. Thus, at this point boiling point will be minimum. Hence, on distilling, first this mixture of constant composition is distilled over then the temperature will rise and other component will pass over.

In such solutions, complete separation of components is not possible. Only a pure component and a minimum boiling azeotropic mixture is obtained.

The azeotropic mixture boiling at minimum temperature than any of its component is called minimum boiling azeotrope.

Example

Ethanol – water forms azeotropic mixture with ethanol 95.6%. It boils at 78.1 °C. This temperature is less than the boiling point of both ethanol (78.5°C) and water (100°C).

Negative Deviations (Maximum Boiling Azeotrope)

Liquid solutions, which have minimum in their vapour pressure curve, shows negative deviations from Raoult's law.

Consider a solution of two components A and B, in which A is more volatile than B.

In fig, at point D the vapour pressure is minimum, hence, boiling point is maximum. At this point liquid mixture distils over without change in composition. It is called maximum boiling azeotrope.

Thus, two components cannot be separated. Only one component and a constant boiling azeotropic mixture is obtained.

The azeotrope boiling at maximum temperature than any of its component is called maximum boiling azeotrope.

Example

HCl – Water system

HCl forms azeotropic mixture with water, which boils at 110°C. It contains 20.24 % HCl.

Saturated Solution

The solution containing maximum amount of solute at a given temperature is called saturated solution.

Unsaturated solution

The solution in which more solute can be dissolved at a given temperature is called unsaturated solution.

Solubility

It is the concentration of solute in solution when it is in equilibrium with the solid substance in its saturated solution at a given temperature.

Solubility is expressed as number of g. of solute in 100g of solvent.

Generally solubility increases with increase in temperature.

Examples

At 0°C, solubility of NaCl in H_2O is 37.5 g / 100 g of H_2O

At 0°C, solubility of $CuSO_4$ in H_2O is 14.3 g / 100 g of H_2O

At 100°C, solubility of $CuSO_4$ in H_2O is 75.4 g / 100 g of H_2O

Explanation

When a solute is dissolved in a solvent, its molecules or ions break away and disperse in the solvent. This is called dissolution.

If solution becomes saturated with solute, then ions or molecules may re-unite to form precipitate. This is called re-crystallization or precipitation.

In a saturated solution, a dynamic equilibrium is established between solid solute and dissolved solute. At this stage rate of dissolution becomes equal to the rate of crystallization.

At this temperature, maximum amount of solute dissolved in solvent is called solubility.

Determination of solubility

- First, a saturated solution of solute is prepared in a given solvent.
- Solution is filtered
- A known volume of this solution is evaporated until solid residue is left behind
- From the mass of residue and volume of solution evaporated, solubility can be calculated.

Solubility Curves

A graphical representation between temperature and solubility of a substance is called solubility curve.

These may be of two types

(I) Continuous Solubility Curves

These are smooth curves and do not show any sharp break points

These may be of two types

(i) Increasing Solubility Curve (ii) Decreasing Solubility Curves

(i) Increasing Solubility Curve

For many substances increase in temperature increases the solubility.

Thus increasing solubility curve is obtained.

Example

Solubility curves of $KClO_3$, $K_2Cr_2O_7$, $Pb(NO_3)_2$ and $CaCl_2$

Solubility curves of NaCl shows only slight increase from 0°C to 100°C

(ii) Decreasing Solubility Curves

For some salts, increase in temperature decreases the solubility of salt.

Thus decreasing solubility curve is produced.

Example

Solubility of $Ce_2(SO_4)_3$ decreases with increase in T upto 40°C. After 40°C it becomes almost constant.

Discontinuous Solubility Curves

These are not smooth and shows sudden breaks due to sudden changes in solubilities

Example

Solubility curve of $Na_2SO_4.10H_2O$, $CaCl_2.6H_2O$ etc.

In these cases, actually a new phase appears at the brak point.

Thus, next curve is the solubility curve of this new phase.

Hence discontinuous solubility curves are actually combinations of two or more continuous solubility curves.

Fractional Crystallization

The separation of solid substances from a solution, one by one, on cooling is called fractional crystallization.

Importance: It is a technique for separation of impurities from chemical products

Explanation: Solubilities of substances depend upon temperature.

e.g. solubility of KNO_3 rapidly changes with temperatrue but solubility of KCl, KBr,

Alanine etc changes gradually.

Thus one substance may precipitate earlier by cooling, leaving behind other in the solution. This is the basis of Fractional Crystallization.

Method: Impure solute is dissolved in hot solvent. In this solvent, solute must be less soluble than impurities.

As the hot solution is cooled, pure solute crystallizes out first leaving impurities in the solution. Thus crude product can be purified.

Exercise Q10. (a)

What are the colligative properties? Why are the called so?

COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS

The properties, which depend upon number of particles and not on their nature, are called colligative properties

Examples

Lowering of Vapour pressure, Elevation in boiling point, Depression in freezing point, Osmotic pressure

Explanation: Why some properties are colligative?

Pure water has definite vapour pressure at a given temperature.

Suppose 6g of urea, 18g of glucose and 34.2g of sucrose are dissolved in 1 kg of H_2O. Each of this is 0.1 molal solution and contain equal number of solute particles. i.e. 1/10 th of Avogadro's particles i.e. 6.02×10^{22}.

In all these cases, lowering of vapour pressure is same. The boiling point of solution is raised by 0.052°C, and freezing point of solution is depressed by 0.186°C than pure H_2O.

Thus lowering of vapour pressure, Elevation in boiling point and Depression in Freezing point are same in all cases due to same number of particles. Hence, these properties are called colligative properties.

Exercise Q10 (b): *What is the physical significance of K_b and K_f values of solvents?*

Molal Boiling Point Constant or Ebullioscopic Constant

It is the elevation in boiling point, which is produced, when 1 mole of solute is dissolved in 1 kg of solvent.

It is denoted by k_b

Example

If 1 mole of solute e.g. urea (60 g), or sucrose (342 g) or glucose (180g) is dissolved in H_2O. The boiling point elevation of water is 0.52 °C. Hence k_b for water is 0.52°C.

Significance: *It tells about how much elevation of boiling point will occur for a particular molality of solution.* ***e.g.*** *for water the elevation in b.p. would be 0.52°C/molal solution.*

Molal Freezing Point Constant or Cryoscopic Constant

It is the depression in freezing point which is produced, when 1 mole of solute is dissolved in 1 kg of solvent.

It is denoted by k_f.

Example

If 1 mole of solute e.g. urea (60 g), or sucrose (342g) or glucose (180g) is dissolved in H_2O. The depression in freezing point of water is 1.86°C. Hence, k_f for water is 1.86°C.

Significance: *It tells about how much depression of freezing point will occur for a particular molality of solution.* ***e.g.*** *for water the depression in f.p. would be 1.86°C/molal solution.*

Table (9.3) K_b and K_f values for some solvents

Solvent	B.P.(°C)	K_b (°C m)	F.P. (°C)	K_f (°C m)
H_2O	100	0.52	0	1.86
Ether	34.4	2.16	-116.3	1.79
Acetic acid	118	3.07	17	3.90
Ethanol	79	1.75	-114.5	1.99

Conditions For Normal Colligative Properties

- Solution must be dilute
- Solute must be non-volatile
- Solute must be non-electrolyte

Study of colligative properties has given a method of molecular mass determination. This study also developed the solution theory.

Q11. ***How do you explain that the lowering of vapour pressure is a colligative property? How do you measure the molar mass of a non volatile, non-electrolyte solute in a volatile solvent?***

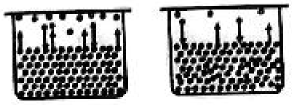
Lowering of Vapour pressure

When a non-volatile, non-electrolyte solute is dissolved in a volatile solvent, its vapour pressure is lowered. This is called lowering of vapour pressure.

Explanation

In pure solvent, all the surface of solvent is covered by solvent molecules.

But when a non-volatile, non-electrolyte solute is added to it to form solution. Some surface is occupied by solute particles. Hence escaping tendency of solvent is decreased, thus its vapour pressure is lowered.



Relationship b/w lowering of vapour pressure and mole fraction of solute

(Application: Determination of Mol. Mass of Solute)

According to Raoults law

Relative lowering of vapour pressure is equal to mole fraction of solute.

i.e. $\frac{\Delta P}{P^0} = x_2$ ____ (1)

Where

ΔP = Lowering of vapour pressure

P^0 = Vapour pressure of pure solvent

x_2 = Mole Fraction of solute

Since $x_2 = \frac{n_2}{n_1 + n_2}$

Where n_2 and n_1 are the number of moles of solute and solvent respectively.

For dilute solutions, n_2 is very small, therefore it can be neglected in the denominator, therefore

$x_2 = \frac{n_2}{n_1}$ ____ (2)

Since $n_1 = \frac{W_1}{M_1}$ and $n_2 = \frac{W_2}{M_2}$, therefore

$x_2 = \frac{n_2}{n_1} = \frac{W_2 M_1}{W_1 M_2}$

Where W_2 = Mass of solute (g)

W_1 = Mass of solvent (g)

M_1 = Mol. Mass of solvent (g)

M_2 = Mol. Mass of solute (g)

Put eq (2) in (1)

$$\frac{\Delta P}{P^0} = \frac{W_2 M_1}{W_1 M_2}$$

or $$M_2 = \frac{P^0}{\Delta P} \times \frac{W_2 M_1}{W_1}$$

Using this equation molecular mass of solute 'M' can be determined.

Example 10

Pure benzene has a vapour pressure of 122 torr at 32°C. When 20 g of a non-volatile solute were dissolved in 300 g of benzene, a vapour pressure of 120 torr was observed. Calculate the molecular mass of the solute. The molecular mass of benzene is 78.1 g/mol.

Solution

Mass of solute 'X' = w_2 = 20 g

Mass of solvent benzene = w_1 = 300 g

Molar Mass of benzene = M_1 = 78.1 g/mol

Vapour pressure of pure ether = P^0 = 122 torr

Vapour pressure of solution = P = 120 torr

Lowering of vapour pressure = $\Delta P = P^0 - P = 122 - 120 = 2$ torr

Molar Mass of 'X' = M_2 = ?

Molar Mass of solute is given by

$$M_2 = \frac{P^0}{\Delta P} \times \frac{w_2 M_1}{w_1}$$

$$M_2 = \frac{122}{2} \times \frac{20 \times 78.1}{300} = \boxed{317.6\ g/mol}$$

Exercise Q14.

Give graphical explanation for elevation of boiling point of a solution. Describe one method to determine the boiling point elevation of a solution.

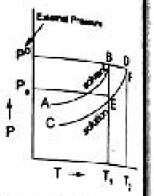
Elevation of Boiling Point

The difference between the boiling points of the solution containing non-volatile non-electrolyte solute, and the pure solvent is known as boiling point elevation of the solution.

It is denoted by ΔT_b

Explanation

A liquid boils at a temperature at which its vapour pressure becomes equal to the external pressure.



Let AB is the vapour pressure-temperature curve of pure solvent. This graph is made by measuring the vapour pressure of pure solvent at different temperatures.

When a non-volatile solute is added to the solvent, the vapour pressure of the resulting solution is lowered, therefore, vapour pressure-temperature curve of solution, CD lies below that of pure solvent.

Let external pressure is $P°$.

It is clear from the graph that solvent attains this pressure at T_1 and starts boiling. However, solution attains this pressure at T_2, which is higher than T_1. Thus, solution boils a higher temperature than pure solvent.

Such that $T_2 - T_1 = \Delta T_b$ = Elevation in boiling point

Generally, higher the conc. of solute, greater will be the lowering of vapour pressure. Hence higher will be the elevation in boiling point.

Thus elevation in boiling point is directly proportional to molality of solution i.e.

$\Delta T_b = k_b \times m$ ___ (1)

Where

ΔT_b = Elevation in boiling point

k_b = Ebullioscopic constant

m = molality of solution

According to eq (1), 6 g of urea or 18 g of glucose in 500 g of water (each is 0.2 molal solution) have same elevation of boiling points. i.e. 0.1°C which is 1/5 th of 0.52°C. So ΔT_b is a colligative property.

Since

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Molecular Mass of solute}} \times \frac{1}{\text{Mass of solvent in Kg}}$$

$$m = \frac{W_2}{M_2} \times \frac{1}{W_1/1000}$$

or $$m = \frac{W_2}{M_2} \times \frac{1000}{W_1} \quad \text{\_\_\_ (2)}$$

Where W_2 = Mass of solute (g)

W_1 = Mass of solvent (g)

M_2 = Molar Mass of solute (g)

Put eq (2) in (1)

$$\Delta T_b = k_b \times \frac{W_2}{M_2} \times \frac{1000}{W_1}$$

or $$M_2 = \frac{k_b}{\Delta T_b} \times \frac{W_2 \times 1000}{W_1}$$

Using this eq. Molar Mass of solute (M_2) can be calculated.

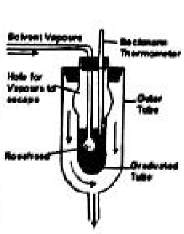
Measurement of Elevation of Boiling Point (Landsberger's Method)

In this method, solution is heated by vapours of boiling solvent

Apparatus

It consists of

- An inner boiling graduated tube with a hole in the side
- A boiling flask, which sends vapours of solvent to the inner tube through a rose head.
- An outer tube, which receive vapours of hot solvent through the hole of inner tube.
- A Beckmann thermometer that can read upto 0.01 K.



Working

A small amount of solvent is placed in the inner boiling tube. It is boiled by the vapours of solvent coming from boiling flask. These vapours boil the solvent in the tube by their latent heat of condensation. When solvent boils its boiling point is noted.

Now supply of vapours is cut off. A weighed quantity of solute is added to the solvent in the inner tube. The boiling point of solution is also noted similarly. The difference of boiling point of solution and solvent gives the elevation in boiling point.

After noting boiling point, volume of solution is also noted to calculate the mass of solvent (w_1).

Molar Mass of solute can be determined by the formula

$$M_2 = \frac{k_b}{\Delta T_b} \times \frac{W_2 \times 1000}{W_1}$$

Example 11

The boiling point of water is 99.725°C. To a sample of 600 g of water are added 24 g of solute having molecular mass 58 g/mol, to form a solution. Calculate the boiling point of solution.

Solution

Mass of solute $= w_2 = 24\ g$

Mass of solvent water $= w_1 = 600\ g$

Molal B.P. constant of water $= k_b = 0.52\ °C$

Molar Mass of solute $= M_2 = 58\ g/mol$

B.P. of pure water $= T° = 99.725\ °C$

Elevation in B.P. $= \Delta T_b = ?$

Elevation in boiling point is given by

$$\Delta T_b = k_b \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$\Delta T_b = 0.52 \times \frac{24}{58} \times \frac{1000}{600} = 0.358\ °C$$

Hence B.P. of solution $= T° + \Delta T_b$

$$= 99.725 + 0.358 = \boxed{100.083\ °C}$$

Exercise Q15:

Freezing points of solutions are depressed when non-volatile solutes are present in volatile solvents. Justify it. Plot a graph to elaborate your answer. Also, give one method to record the depression of freezing point of a solution.

Depression of Freezing Point

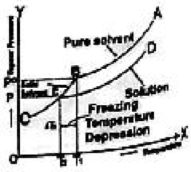
The difference in the freezing point of solution containing non-volatile, non-electrolyte solute and pure solvent is called depression in freezing point.

It is denoted by ΔT_f

Explanation

Freezing point of a liquid is defined as the T at which solid and liquid phases have same vapour pressures.

At freezing point both liquid and solid phases are in equilibrium.



Consider the vapour pressure– temperature curves of pure solid solvent 'BC' (sublimation curve), pure liquid solvent 'AB' and solution 'ED' as shown in the fig.

Vapour pressure curve of solid solvent is more steep showing that the change in vapour pressure is more rapid with temperature.

Since vapour pressure of solution curve is lower than that of pure solvent, therefore, its vapour pressure–temperature curve is below that of pure solvent.

At freezing point of solvent both solid and liquid phases are in equilibrium and have same vapour pressure. It occurs at point B, so it is the freezing point of pure solvent.

At freezing point of solution both solid solvent and liquid solution are in equilibrium and have same vapour pressure. It occurs at point E. So it is the freezing point of solution.

Since $T_1 > T_2$, therefore solution freezes at lower temperature that that of pure solvent. Such that

$$\Delta T_f = T_1 - T_2$$

The depression in freezing point is directly proportional to molality of solution i.e. $\Delta T_f \propto m$

$$\Delta T_f = k_f \times m \quad \text{\_\_\_(1)}$$

Where

ΔT_f = Depression in freezing point

k_f = Cryoscopic constant

m = Molality of solution

$$\text{Since Molality} = \frac{\text{Mass of solute}}{\text{Molecular Mass of solute}} \times \frac{1}{\text{Mass of solvent in Kg}} \text{ oOr}$$

$$m = \frac{W_2}{M_2} \times \frac{1}{W_1/1000}$$

or $$m = \frac{W_2}{M_2} \times \frac{1000}{W_1} \quad \text{\_\_\_\_(2)}$$

Where W_2 = Mass of solute (g)

W_1 = Mass of solvent (g)

M_2 = Molar Mass of solute (g)

Put eq (2) in (1)

$$\Delta T_f = k_f \times \frac{W_2}{M_2} \times \frac{1000}{W_1}$$

or $$M_2 = \frac{k_f}{\Delta T_f} \times \frac{W_2 \times 1000}{W_1}$$

Using this equation Molar Mass of solute (M_2) can be calculated.

Measurement of Depression in Freezing Point (Beckmann's method)

Apparatus

It consists of

- A freezing tube with a side arm fitted with a Beckmann thermometer. It has stirrer and contains solvent or solution.
- An outer tube surrounding the inner tube. Space between outer and inner tube behave as air jacket for slower and uniform rate of cooling.
- An outer vessel containing freezing mixture e.g. ice and water with stirrer.

Figure: Beckmann's freezing point apparatus

Working

About 20–25 g of solvent is taken in the freezing tube. The bulb of thermometer is dipped in the solvent. First, an approximate freezing point of solvent is determined by directly cooling the tube in freezing mixture.

Freezing tube is then taken out. After re-melting solvent, it is then placed in air jacket and cooled slowly and accurate freezing point of solvent is noted.

Now about 0.2 g to 0.3 g of solute is added to the solvent. The freezing point of solution is determined by stirring the solution.

The difference of freezing points of solution and solvent gives the depression in freezing point.

Molar Mass of solute can be determined by the formula

$$M_2 = \frac{k_f}{\Delta T_f} \times \frac{W_2 \times 1000}{W_1}$$

Example 12

The freezing point of pure camphor is 178.4°C. Find the freezing point of a solution containing 2 g of a non-volatile compound, having molecular mass 140, in 40 g of camphor. The molal freezing point constant of camphor is 37.7 °C kg /mol.

Solution

Mass of solute compound $= w_2 = 2$ g
Mass of solvent camphor $= w_1 = 40$ g
Molal F.P. constant of camphor $= k_f = 37.7\ ^\circ C$ kg/mol
Molecular Mass of solute $= M_2 = 140$ g/mol

Freezing point of pure camphor $= T^\circ = 178.4\ ^\circ C$
Freezing point depression $= \Delta T_f = ?$
Freezing point of solution $= ?$

Depression in F.P. is given by

$$\Delta T_f = k_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1}$$

$$\Delta T_f = 37.7 \times \frac{2}{140} \times \frac{1000}{40} = 13.46^\circ C$$

Hence F.P. of solution $= T^\circ - \Delta T_f$
$= 178.4 - 13.46 = \boxed{164.94\ ^\circ C}$

Applications of B.P. Elevation and F.P. Depression

- **Preparation of antifreeze**

In winter, water in radiators of automobile may freeze. To protect this a solute ethylene glycol is added to it. It is completely miscible with H_2O. It is also almost non-volatile. Thus it depresses the freezing point of H_2O. Hence, it prevents the freezing of water in winter.

In summer, it protects the radiator from boiling over.

- **Preparation of Freezing mixture**

When NaCl or KNO_3 is added to H_2O, its freezing point is lowered. This mixture is used as freezing mixture in an ice-cream machine.

Exercise Q16:

Discuss the energetics of solution. Justify the heats of solutions as exothermic and endothermic properties.

ENERGETICS OF SOLUTION

The amount of heat absorbed or evolved when a substance is dissolved in a solvent to form a solution is called heat of solution.

The enthalpy of a solution of a substance is defined as the heat changed when one mole of a substance is dissolved in a specified number of moles of solvent at a given temperature.

It is denoted by ΔH_{soln}. It is the heat of solution at infinite dilution

Example

When 1 mole of NaCl (58.5g) is dissolved in 10 moles of H_2O (180g), 2.008 kJ energy is absorbed.

$$NaCl_{(s)} + 10H_2O \longrightarrow NaCl(10H_2O) \qquad \Delta H = +\ 2.008\ KJ/mol$$

Explanation

(i) When a solute is dissolved in solvent, following things occur. Molecules of solvents move away from each other. This process requires energy to overcome the cohesive intermolecular forces, hence it is endothermic.

(ii) Solute molecules separate from each other. This process also requires energy hence it is also endothermic.

Table : Heats of solution of some ionic solids	
Substance	Heat of solution kJ mol⁻¹
NaCl	4.98
NH_4NO_3	26.0
KCl	17.8
KI	21.4

(iii) Solute and solvent particles develop forces for each other and energy is released. It is an exothermic process.

The exothermic or endothermic nature of process depends upon the strength of two types of forces.

The process of dissolution occurs with either absorption or release of energy. This is due to breaking and remaking of intermolecular forces between solute and solvent.

Examples

When KNO_3 is dissolved in water, Temperature is decreased showing endothermic process

When LiCl is dissolved in H_2O, Temperature is increased. Thus it is exothermic process.

Mathematically

$\Delta H_{soln} = H_{solution} - H_{components}$

Where ΔH_{soln} = Enthalpy of solution

$H_{solution}$ = Heat content of solution after formation

$H_{components}$ = Heat content of components before mixing

Both $H_{components}$ and $H_{solution}$ can not be calculated

Only ΔH_{soln} can be calculated

ΔH_{soln} is –ve when $H_{solution} < H_{components}$

ΔH_{soln} is +ve when $H_{solution} > H_{components}$

Hydration energy of ions

When an ionic compound is dissolved in solvent. Some forces develop between ionic solid and solvent. This process releases energy. This energy realeased ultimatey breaks the lattice of ionic solid and it dissolves.

Example

Dissolution of KI in H_2O takes place in two steps

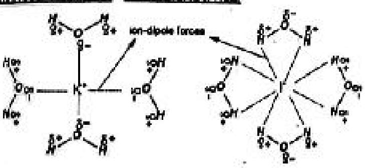
- In first step lattice of KI is broken down due to solute – solvent interaction. This process requires energy hence it is endothermic. The energy required to break lattice is called lattice energy.

The process is

$$KI \longrightarrow K^+ + I^-$$

Lattice energy of ionic solids is always greater than molecular solids.

Dissolution of KI in Water



Ion	[illegible]
H^+	–1075
Li^+	–499
Na^+	–390
Ag^+	–464
K^+	–305
Mg^{2+}	–1891
Cu^{2+}	–1562
NH_4^+	–281
F^-	–457
Cl^-	–384
Br^-	–351
OH^-	–460

In second step, K^+ and I^- ions produced are surrounded by dipoles of water. This process is called hydration or solvation. During this process, energy is released. It is called heat of hydration, e.g.,

$$K^+ + I^- + xH_2O \longrightarrow K^+_{(aq)} + I^-_{(aq)}$$

Thus, overall process is

$$KI + xH_2O \longrightarrow K^+_{(aq)} + I^-_{(aq)}$$

Different ions have different heats of hydration

Effect of Ionic size on Hydration Energy

Generally greater the ionic radii of monopositive ions, smaller is the heat of hydration and vice versa.

Divalent and Trivalent ions have greater heat of hydration due to large charge densities.

Anions also show similar trend.

Infinite Dilution

On adding more H_2O to NaCl solution, further heat change may occurs. This heat change depends upon the amount of water used for dilution. The heat of dilution slowly decreases and finally no further heat change occurs. This occurs, when there are 800 – 1000 moles of water to one mole of solute. This is called infinite dilution

Thus heat of solution at infinite dilution will be

$$NaCl_{(s)} + H_2O \longrightarrow NaCl_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)} \quad \Delta H_{soln} = +4.90\ kJ/mol$$

HYDRATION AND HYDROLYSIS

HYDRATION

The process in which water molecules surround and interact with the solute particles without breaking any O – H bond is called hydration

Explanation

Water is an excellent solvent. It dissolves various ionic substances because of hydration of ions. A hydrated ion is a cluster of ions and one or more water molecules.

In solution, each ion is surrounded by indefinite no. of water molecules.

However, when water solution of a salt is evaporated, the salt crystallizes out with definite no. of water molecules. These water molecules are called water of crystallization and are present in crystal lattice of salt. During this process no bonds are broken. However, new bonds are formed.

In ionic substances, negative ions are bigger and positive ions are smaller in size. Thus negative ions have low charge density (charge per unit volume), while positive ions have high charge density.

Generally, ions with smaller size and high charge dinsity (i.e. +ive ions) have more attraction for polar water molecules than –ve ions. Thus, in $CuSO_4 . 5H_2O$, out of five water molecule, four are attached with smaller Cu^{2+} ion and one is attached with SO_4^{2-} ion.

Hydrates

The crystalline substance, containing chemically combined H_2O in definite proportions is called hydrate

Examples

$CuSO_4 . 5H_2O$, $Na_2SO_4 . 10H_2O$

In $CuSO_4 . 5H_2O$, four H_2O are attached with Cu^{2+} and one with SO_4^{2-}

Preparation of Hydrate

Hydrates are prepared by evaporating their aqueous solutions.

Hydrates are not limited to salts. Acids, bases and elements also form hydrates.

Water of Crystallization

The water molecules, which are attached with compound when crystallised from its solution, are called water of crystallization.

Example

$(COOH)_2 . 2H_2O$ (Oxalic acid)	$BaCl_2 . 2H_2O$
$MgCl_2 . 6H_2O$	$Na_2CO_3 . 10H_2O$
$MgSO_4 . 7H_2O$ (Epsom salt)	$CaSO_4 . 2H_2O$ (Gypsum)
$Na_2B_4O_7 . 10H_2O$ (Borax)	

HYDROLYSIS

The process in which water reacts chemically with the added solute is called hydrolysis

Explanation

A salt produces cations and anions on dissolving in water. These ions may react with water to produce acidic or basic solution.

Cation hydrolysis produces acidic solution

$$M^+ + H\text{-}OH \rightleftharpoons MOH + H^+ \text{(acidic solution)}$$

Anion hydrolysis produces basic solution

$$A^- + H\text{-}OH \rightleftharpoons AH + OH^- \text{(basic solution)}$$

Generally, salts may be classified into four types.

1. *Salts Of Weak Base With Strong Acids.*

e.g. $CuSO_4$ .It ionizes as

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO_4^{2-}$$

$$Cu^{2+} + 2H\text{-}OH \rightleftharpoons Cu(OH)_2 + 2H^+$$

Thus aq. solution of $CuSO_4$ is acidic.

Other Examples

$$AlCl_3 + 3H_2O \rightleftharpoons Al(OH)_3 + 3H^+ + 3Cl^-$$

$$NH_4Cl + H_2O \rightleftharpoons NH_4OH + H^+ + Cl^-$$

Thus, these hydrolysis reactions produce weak bases and strong acids. Both Cl^- and SO_4^{2-} are weak conjugate bases of strong acids HCl and H_2SO_4 respectively. Thus they are not hydolyzed by water. The H^+ are free in solution, therefore, their solutions are acidic in nature. The K_a values are of HCl and H_2SO_4 are very high as compared to K_b values of $Al(OH)_3$, NH_4OH and $Cu(OH)_2$.

2. *Salts Of Strong Base With Weak Acid.*

e.g. CH_3COONa . It ionizes as

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

CH_3COO^- hydrolyze in water to produce basic solution.

$$CH_3COO^- + H\text{-}OH \rightleftharpoons CH_3COOH + OH^-$$

Thus aq. solution of CH_3COONa is basic.

<u>Other Examples</u>

Na_3PO_4 , Na_3AsO_4 etc

These also give basic solution due to formation of Na^+ and OH^- and weak acids H_3PO_4 and H_3AsO_4 respectively, which are not ionized.

3. Salts Of Weak Base With Weak Acid

By adding such salt in water, resulting solution may be acidic, basic or neutral depending upon the pK_a and pK_b values of acid and base produced.

<u>Examples</u>

CH_3COONH_4, NH_4CN etc.

4. Salts Of Strong Acid With Strong Base

e.g. NaCl ionizes as

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

Both Na^+ and Cl^- are not hydrolyzed by H_2O, therefore, it's solution will be neutral. Thus salts of strong acids and strong bases are not hydrolyzed by water.

<u>Other Examples</u>

Na_2SO_4 , KBr, KCl etc.

Thus, salts of strong acid and strong bases are not hydrolyzed by water.

Difference between Hydration and Hydrolysis

	HYDRATION		HYDROLYSIS
1	The process in which water molecules surround and interact with the solute particles without breaking any bond is called hydration	1	The process in which water reacts chemically with the added solute is called hydrolysis
2	Largely physical interactions occur between solute and water molecules.	2	Chemical reaction occurs between solute particles and water molecules.
3	Old bonds are not broken but new bonds may be formed.	3	Old bonds are broken and new bonds are formed.
4	This process does not change the pH of the solution	4	This process may change the pH of solution.

OBJECTIVE AND SHORT ANSWER QUESTIONS EXERCISE

Q.1 Multiple Choice Questions

(i) Molarity of pure water is

(a) 1 (b) 18 (c) 55.5 (d) 6

(D.G. Khan Board, 2009) (Rawalpindi Board, 2010) (D.G. Khan Board, 2012) (Multan Board, 2011, 2012) (Sargodha Board, 2011) (Gujranwala board, 2014) (Lahore board, 2014)

(ii) 18 g of glucose is dissolved in 90 g of water. The relative lowering of vapour pressure is equal to

(a) 1/5 (b) 5.1 (c) 1/51 (d) 6

(Rawalpindi board, 2012) (Gujranwala board, 2008, 2013)

(iii) A solution of glucose is 10%. The volume in which 1 g mole of it is dissolved will be

(a) 1 dm^3 (b) 1.8 dm^3 (c) 200 cm^3 (d) 900 cm^3

(D.G. Khan Board, 2012) (Sargodha Board, 2012)

(iv) An aqueous solution of methanol in water has vapour pressure.

(a) equal to that of water (b) equal to that of methanol

(c) more than that of water (d) less than that of water

(Bahawalpur Board, 2010) (Sargodha Board, 2013)

(v) An azeotropic mixture of two liquids boils at a lower temperature than either of them when (Faisalabad Board, 2009)

(a) It is saturated

(b) It shows positive deviation from Raoult's law

(c) It shows negative deviation from Raoult's law

(d) It is metastable

(vi) In azeotropic mixture showing positive deviation from Raoult's law, the volume of the mixture is

(a) Slighltly more than the total volume of the components

(b) Slighltly less than the total volume of the components

(c) Equal to the volume of the components

(d) None of these

(vii) Which of the following solutions has the highest boiling point?

(a) 5.85 % solution of NaCl (b) 18 % solution of glucose

(c) 6 % solution of urea (d) all have the same boiling point

(D.G. Khan Board, 2009) (Multan Board, 2010) (Sargodha Board, 2010) (Lahore board, 2013)

(viii) Two solutions of NaCl and KCl are prepared separately by dissolving same amount of the solute in water. Which of the following statements is true for these solutions

(a) KCl solution will have higher boiling point than NaCl solution

(b) Both the solutions have different boiling point.

(c) KCl and NaCl solutions possess same vapour pressure.

(d) KCl solution possesses lower freezing point than NaCl solution.

(Multan Board, 2011)

(ix) The molal boiling point constant is the ratio of the elevation in boiling point to

(a) molarity (b) molality (c) mole fraction of solvent (d) mole fraction of solute

(Sargodha Board, 2009, 2014)

(x) Colligative properties are the properties of

(a) Dilute solutions which behave as nearly ideal solutions
(b) Concentrated solutions which behave as nearly non-ideal solutions
(c) Both (a) and (b)
(d) Neither (a) nor (b)

(Bahawalpur Board, 2009) (Rawalpindi Board, 2009)

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (c)

Consider 1 dm^3 of water
1 dm^3 of water = 1 kg = 1000 g
Molecular mass of water = 18 g mol −1
Thus

Number of moles of water in 1 $dm^3 = \frac{1000}{18}$ = 55.55 moles

Since 55.55 moles of water are present in 1 dm^3, therefore, molarity of pure water is 55.55.

(ii) Ans: (c)

Mass of glucose = 18 g
Molecular mass of glucose = 180 g

No. of moles of glucose $= \frac{18}{180} = 0.1$ moles

Mass of water = 90 g
Molecular mass of water = 18 g

No. of moles of water $= \frac{90}{18} = 5$ moles

Thus mole fraction of glucose $= x_2 = \frac{0.1}{5 + 0.1} = \frac{1}{51}$

According to Raoult's law

$$\frac{\Delta P}{P^o} = x_2 = \frac{1}{51}$$

(iii) Ans: (b)

1 g mole of glucose = 180 g
10% solution means 10 g of glucose are present in 100 cm^3 of solution. Thus
10 g of glucose are present in solution = 100 cm^3
180 g of glucose will be present in solution

$= \frac{100 \times 180}{10} = 1800\ cm^3 = 1.8\ dm^3$

(iv) Ans: (c)

Ethanol and water forms a non-ideal solution. This solution shows positive deviations from Raoult's law. Hence, vapour pressure of this solution will be more than that of water.

(v) Ans: (b)

If an azeotropic mixture of two liquids boils at lower temperature than either of them, then it means that vapour pressure of this mixture is more than the ideal vapour pressure. Hence, this mixture will show positive deviations from Raoult's law.

(vi) Ans: (a)

In the formation of solution that shows positive deviation from Raoult's law, forces of attractions among molecules are decreased. Therefore, molecules tend to remain away from each other. Hence, volume of solution is increased.

(vii) Ans: (a)

Elevation in boiling point is a colligative property and is directly proportional to the number of particles in the solution.
5.85% NaCl, 18% glucose and 6.0% urea solutions are all 1 molal solutions. However, NaCl ionizes in water to give double number of ions. Due to greater number of particles in NaCl solution, its boiling point will be highest.

(viii) Ans: (c)

Both NaCl and KCl ionizes in water completely to give double number of ions. When same moles of NaCl and KCl are dissolved separately in fixed amount of water, they produce same number of ions in water. Hence, both these solutions will have same values of colligative properties like vapour pressure lowering etc.

(ix) Ans: (b)

Elevation in boiling point is given as

$\Delta T_b = k_b \times m$ or $\frac{\Delta T_b}{m} = k_b$.

Hence, molal boiling point constant (kb) is the ratio of the elevation in boiling point (Δ Tb) to the molality of solution (m).

(x) Ans: (a)

In dilute solutions, particles do not have forces of attractions among themselves. Therefore, the solutions behave ideally and colligative properties are observed

Fill in the blanks with suitable words

(i) Number of molecules in 1 dm^3 of 1 M sugar solution is ____.
(ii) 100 g of a 10% aq. solution of NaOH contains 10 g of NaOH in ____ g of water.
(iii) When an azeotropic mixture is distilled, its ____ remains constant.
(iv) The molal freezing point constant is also known as ____ constant
(v) The boiling point of an azeotropic solution of two liquids is lower than either of them because the solution shows ____ from Raoult's law.
(vi) Among equimolal aq. solutions of NaCl, $BaCl_2$ and $FeCl_3$, the maximum depression in freezing point is shown by ____ solution.
(vii) A solution of ethanol in water shows ____ deviations and gives azeotropic solution with ____ boiling point than other components.
(viii) Colligative properties are used to calculate ____ of a compound.
(ix) The hydration energy of Br^- ion is ____ than F^- ion
(x) The aqueous solution of NH_4Cl is ____ while that of Na_2SO_4 is ____.

Answers

(i) 6.02 X 10 (ii) 90 g (iii) compostion (iv) cryoscopic
(v) positive deviations (vi) $FeCl_3$ (vii) positive, lower
(viii) molar mass (ix) less (x) acidic, neutral

Indicate True or False from the given statements

(i) At a definite temperature, the amount of a solute in a saturated solution is fixed.
(ii) Polar solvents readily dissolve non-polar covalent compounds.
(iii) The molecular mass of an electrolyte determined by lowering of vapour pressure is less than the theoretical molecular mass.
(iv) The rate of evaporation of a liquid is inversely proportional to the intermolecular forces of attraction.
(v) The solubility of a substance decreases with increase in Temperature if the heat of a solution is negative.
(vi) The rate of evaporation of a liquid is inversely proportional to the intermolecular forces of attraction.
(vii) All solutions containing 1 g of non-volatile, non-electrolyte solutes in same solvent will have the same freezing point.
(vii) The freezing point of a 0.05 molal solution of a non-electrolyte in water is −0.93 ^oC.
(ix) Hydration and hydrolysis are different process for Na_2SO_4
(x) The hydration energy of an ion only depends upon its charge.

Answers

True (ii) False (iii) True (iv) True (v) True
True (vii) False (viii) False (ix) False (x) False

Q4. Define and explain the followings with one example in each case.

(a) A homogeneous phase **(b) Zeotropic solutions**

(c) A concentrated solution **(d) Heat of hydration**

(e) A solution of solid in a solid **(f) Water of crystallization**

(g) A consulate temperature **(h) Azeotropic solution**

(i) A non-ideal solution **(j) Conjugate solution**

Solved in the chapter

Q5 (a) What are the concentration units of solutions. Compare molar and molal solutions.

Solved on Page 504

(b) One has one molal solution of NaCl and one molal solution of glucose.

(i) Which solution has greater number of particles of solute?

NaCl dissociates in H_2O, while glucose is not ionized. NaCl produces Na^+ and Cl^- ions. Thus number of particles are increased. Hence, 1 molal NaCl solution contain greater number of particles than 1 molal glucose solution.

(ii) Which solution has greater amount of the solvent

Both are 1 molal solution i.e. 1 mole of solute is dissolved in 1 kg of solvent. Therefore both will have same amount of solvent.

(iii) How do we convert these concentrations into weight by weight percentage?

For 1 molal NaCl solution	For 1 molal glucose solution
Moles of NaCl = 1	Mass of glucose dissolved = 180 g
Mass of NaCl = 58.5 g	Mass of solvent (water) = 1000 g
Since 1 mole of NaCl is dissolved in 1 kg of solvent, therefore	Total mass of solution = 1000 + 180 = 1180 g
Mass of solvent (water) = 1000 g	% of glucose = $\frac{\text{Mass of glucose}}{\text{Total mass of solutoin}} \times 100$
Total mass of the solution = 1000 + 58.5 = 1058.5	% of glucose = $\frac{180}{1180} \times 100 = \boxed{15.2\%}$
% of NaCl = $\frac{\text{Mass of NaCl}}{\text{Total mass of solution}} \times 100$	
% of NaCl = $\frac{58.5}{1058.5} \times 100 = \boxed{5.52\%}$	

Q6. Explain the following with reasons

(i) The concetration in terms of molality is independent of temperature but molarity depends upon temperature.

(Rawalpindi Board, 2007: Gujranwala Board, 2009: Faisalabad Board, 2007, 2011: Multan Board, 2011)

OR Why the concentration of a molar solution is changed by variation of temperature

(D.G. Khan Board, 2008)

Molality is defined as the number of moles of solute dissolved in 1 kg of solvent, while

Molarity is defined as the number of moles of solute dissolved in 1 dm^3 of solution.

Since molality is based upon mass, therefore, it is independent of temperature. While molarity is based upon volume, therefore, it varies with temperature due to change in volume.

(ii) The sum of mole fractions of all the components is always equal to unity for any solution.

(Faisalabad Board, 2008, 2013: Lahore Board, 2010: D.G. Khan Board, 2012: Multan Board, 2012)

OR Prove that sum of mole fractions of all components is always equal to one. *(Rawalpindi Board, 2008)*

Consider a solution of two components A and B

Let moles of A are n_A and that of B are n_B

Their mole fractions are given by

$$x_A = \frac{n_A}{n_A + n_B} \quad \_\_(1) \qquad x_B = \frac{n_B}{n_A + n_B} \quad \_\_(2)$$

Their sum of mole fractions will be

$$x_A + x_B \quad \_\_(3)$$

Put eq (1) and (2) in eq (3)

$$\frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B}$$

or

$$\frac{n_A + n_B}{n_A + n_B} = 1$$

Hence, sum of mole fractions of different components in a solution is equal to one.

(iii) 100 g of 98% H_2SO_4 has a volume of 54.38 cm^3

98% H_2SO_4 has a density $= d = 1.84\ g/cm^3$

Mass of H_2SO_4 $= m = 100\ g$

Volume of H_2SO_4 $= V = ?$

Since $d = \frac{m}{V}$

or $V = \frac{m}{d} = \frac{100}{1.84} = 54.38\ cm^3$

(iv) *Relative lowering of vapour pressure is independent of the temperature.*
(Faisalabad Board, 2008: Sargodha Board, 2009: Rawalpindi Board, 2009: Gujranwala Board, 2012)

According to Raoult's law

Relative lowering of vapour pressure is equal to the mole fraction of solute

i.e. $\frac{\Delta P}{P^0} = x_2$

Where $\frac{\Delta P}{P^0}$ = Relative lowering of vapour pressure

While $x_2 = \frac{n_2}{n_1 + n_2}$ = mole fraction of solute

Since number of moles are not changed with temperature. Hence, relative lowering of vapour pressure is independent of temperature.

(v) *Colligative properties are obeyed when the solute is non-electrolyte.*

Colligative properties depend upon number of solute particles. If solute is electrolyte then it will ionize and change the number of particles in the solution. Hence, abnormal colligative properties will be observed.

(vi) *Colligative properties are obeyed when the solutions are dilute.*
OR Colligative properties are obeyed when the solute is non-electrolyte and also when the solutions are dilute. Explain with reason. (Gujranwala Board, 2009: Rawalpindi Board, 2012: Multan Board, 2013)

Colligative properties also depend on the fact that solution should be dilute so that every solute particle behave independently.

In conc. solution, solute particles don't behave independently. They have attraction for each other. Thus, normal colligative properties are only observed when the solution is dilute.

(vii) *The total volume of the solution by mixing 100 cm^3 of water with 100 cm^3 of alcohol may not be equal to 200 cm^3. Justify it.*

During ideal solution formation volume is not changed. However, Alcohol and water form a non-ideal solution. Forces of attraction between water and alcohol in pure state are greater than in solution. Thus, it shows positive deviation from Raoults law. During the formation of this solution heat is absorbed and volume changes.

Hence 100 cm^3 of H_2O and 100 cm^3 of alcohol may not be equal to 200 cm^3.

(viii) *One molal solution of urea in water is dilute as compared to one molar solution of urea, but the number of particles of the solute is same. Justify it.*
(Faisalabad Board, 2007, 2010: Azad Kashmir Board, 2013)

OR One molal glucose solution is dilute as compared to one molar solution of glucose. Why?
(Multan Board, 2008: Faisalabad Board, 2009: Rawalpindi Board, 2011: Gujranwala Board, 2011: Lahore Board, 2013: Sargodha Board, 2014)

OR Why a molar solution is more concentrated than a molar solution? *(Multan Board, 2010)*

Both 1 molal and 1 molar urea solution contain 1 mole of urea. Hence both these solutions contain same number of particles i.e. 6.02×10^{23}.

For 1 molal solution, 1 mole of urea is dissolved in 1 kg of water i.e. 1 dm^3

However,

For 1 molar solution, 1 mole of urea is first taken in a measuring flask and then volume is made up to 1 dm^3.

Hence, 1 molar solution contain less amount of H_2O than 1 molal solution.

Q7. *What are non-ideal solutions? Discuss their types and give three example of each.*

Q8. *(a) Explain fractional distillation. Justify the two curves when composition is plotted against boiling point of solutions.*

(b) The solutions showing positive and negative deviations cannot be fractionally distilled at their specific compositions. Explain it.

Q9. *(a) What are azeotropic mixtures? Explain them with the help of graphs?*
OR What are azeotropes (or azeotropic mixture)? Give one example.
(D.G. Khan Board, 2007: Multan Board, 2009: Lahore Board, 2010: Bahawalpur Board, 2012: Sargodha Board, 2012, 2014)

(b) Explain the effect of temperature on phenol-water system.
Solved on Page 514

Q10. *(a) What are the colligative properties? Why are the called so?* *(D.G. Khan Board, 2007: Lahore Board, 2009: Multan Board, 2010: Rawalpindi Board, 2012)*
OR Why some properties are called colligative? *(Sargodha Board, 2010: D.G. Khan Board, 2011: Bahawalpur Board, 2012)*
Solved on Page 524

(b) What is the physical significance of K_b and K_f values of solvents?
Solved on Page 524

Q11. *How do you explain that the lowering of vapour pressure is a colligative property? How do you measure the molar mass of a non volatile, non-electrolyte solute in a volatile solvent?*
Solved on Page 525

Q12 How do you justify that

(a) Boiling points of the solvents increase due to the presence of solutes
(Faisalabad Board, 2007; Gujranwala Board, 2010; Multan Board, 2013; Lahore Board, 2014)

OR Why the boiling points of a solution of a non-volatile solute in a volatile solvent is always greater than the boiling point of pure solvent? *(Gujranwala Board, 2008)*

When a non-volatile, non-electrolyte solute is dissolved in volatile solvent, its vapour pressure is lowered. Thus to boil solution more heat is required to bring its vapour pressure equal to external pressure. Hence, boiling point of solution is increased.

(b) Freezing points are depressed due to the presence of solutes
(Lahore Board, 2007, 2009; Faisalabad Board, 2010, 2011; Rawalpindi Board, 2011; Gujranwala Board, 2012)

OR Why the freezing point of the solution is always less than the freezing point of pure solvent? *(Faisalabad Board, 2009)*

When a non-volatile, non-electrolyte solute is dissolved in volatile solvent, its vapour pressure is lowered. Due to lowering of vapour pressure, solution freezes below the freezing point of pure solvent. Hence, freezing point of solution is depressed.

(c) The boiling point of one molal urea solution is 100.52 °C but the boiling point of two molal urea solution is less than 101.04 °C.

Elevation of boiling point is a colligative property. Normal colligative properties are observed when the solution is dilute so that each solute particle behave independently.

Two molal urea solution is conc. than one molal solution. In concentrated two molal solution, solute particles do not behave independently. They have attractions for each other. Hence one molal solution boils at 100.52°C. While two molal solution boils abnormally below expected at 101.04°C.

(d) Beckmann thermometer is used to note the depression in freezing point.
(Rawalpindi Board, 2007; Multan Board, 2009; Lahore Board, 2013; Bahawalpur Board, 2011)

There is very small difference between freezing point of pure solvent and its dilute solution. Ordinary thermometer can read upto 0.5 K (upto one decimal place). Hence these cannot differentiate between freezing point of pure solvent and solution.

Beckmann thermometer can read upto 0.01 K (upto two decimal places). Hence it can exactly measure the freezing point of pure solvent and solution.

(e) In summer the antifreeze solutions protect the liquid of the radiator from boiling over. *(Rawalpindi Board, 2007)*

Antifreeze solution consists of solution of ethylene glycol in H_2O. Since ethylene glycol is non-volatile, therefore, vapour pressure of this solution is lowered and boiling point is increased.

In summer, due to large heat in engine, H_2O may boil over in radiator. However, due to lower vapour pressure of solution, it requires much greater heat to boil. Hence, this mixture prevents boiling over of H_2O.

(f) NaCl or KNO_3 are used to lower the melting point of ice. *(Sargodha Board, 2007; Gujranwala Board, 2008, 2011) (Lahore Board, 2013; Sargodha Board, 2013; Multan Board, 2013)*

When NaCl or KNO_3 is added to H_2O, its vapour pressure is lowered. Due to lowering of vapour pressure, solution freezes below the freezing point of H_2O, so it will have more cooling effect.

Hence, this mixture is used as freezing mixture e.g. in an ice-cream machine

Q13. *What is Raoult's law. Give its three statements. How this law can help us to understand the ideality of a solution.*

Solved on Page 515

Q14. *Give graphical explanation for elevation of boiling point of a solution. Describe one method to determine the boiling point elevation of a solution.*

Solved on Page 527

Q15. *Freezing points of solutions are depressed when non-volatile solutes are present in volatile solvents. Justify it. Plot a graph to elaborate your answer. Also, give one method to record the depression of freezing point of a solution.*

Solved on Page 530

Q16. *Discuss the energetics of solution. Justify the heats of solutions as exothermic and endothermic properties.*

Solved on Page 533

IMPORTANT FORMULAS

% by weight

$$\%\text{ by weight} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

Molarity

$$M = \frac{\text{No. of moles of solute}}{\text{Volume of solution in } dm^3}$$

$$M = \frac{\text{wt. of solute}}{\text{Molecular wt. of solute}} \times \frac{1}{\text{Volume of solution in } dm^3}$$

Amount/dm^3 of a substance = Molarity × Molar Mass

Molality

$$m = \frac{\text{No. of moles of solute}}{\text{Weight of solvent in kg}}$$

$$m = \frac{\text{wt. of solute}}{\text{Molecular wt. of solute}} \times \frac{1}{\text{Weight of solvent in kg}}$$

Mole Fraction

$$x = \frac{\text{No. of moles of one compponent}}{\text{Total no. of moles of all components of solution}}$$

Parts Per Million (ppm)

$$ppm = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6$$

Raoult's law

$$P = P^o x_1 \quad \text{or} \quad \Delta P = P^o x_2 \text{ or } \frac{\Delta P}{P^0} = x_2$$

Lowering of V.P./Mol. Mass determination etc.

$$\frac{\Delta P}{P^0} = \frac{w_2 M_1}{w_1 M_2} \quad \text{or} \quad M_2 = \frac{P^0}{\Delta P} \times \frac{w_2 M_1}{w_1}$$

Elevation of B.P./ Mol. Mass determination etc.

$$\Delta T_b = k_b \times m \quad \text{or} \quad \Delta T_b = k_b \times \frac{w_2}{M_2} \times \frac{1000}{w_1} \quad \text{or } M_2 = \frac{k_b}{\Delta T_b} \times \frac{w_2 \times 1000}{w_1}$$

and Boiling point of solution = Boiling point of solvent + ΔT_b

Depression of F.P./ Mol. Mass determination etc.

$$\Delta T_f = k_f \times m \quad \text{or} \quad \Delta T_f = k_f \times \frac{w_2}{M_2} \times \frac{1000}{w_1} \quad \text{or } M_2 = \frac{k_f}{\Delta T_f} \times \frac{w_2 \times 1000}{w_1}$$

and Freezing point of solution = Freezing point of solvent − ΔT_f

NUMERICAL PROBLEMS (EXERCISE)

Q.17 ***(a) Calculate the molarity of glucose solution when 9 g of it is dissolved in 250 cm³ of solution.***

Solution:

Mass of glucose = w = 9 g
Mol. Mass of glucose = M = 180 g

Volume of solution = V = 250 cm³ = $\frac{250}{1000}$ dm³ = 0.25 dm³

Molarity of solution = ?

Molarity of solution is given by

$$\text{Molarity} = \frac{w}{M} \times \frac{1}{V(dm^3)}$$

$$\text{Molarity} = \frac{9}{180} \times \frac{1}{0.25} = \boxed{0.2\ mol/dm^3}$$

(b) Calculate the mass of urea in 100 g of water in 0.3 molal

Solution

Mass of water (solvent) = W = 100 g = $\frac{100}{1000}$ = 0.1 kg

Molality of solution = m = 0.3
Molar mass of urea = M = 60 g/mol
Mass of urea dissolved = w = ?

Molality is given by

$$m = \frac{w}{M} \times \frac{1}{W(kg)}$$

$$0.3 = \frac{w}{60} \times \frac{1}{0.1}$$

or $w = 0.3 \times 60 \times 0.1 = \boxed{1.8\ g}$

(c) Calculate the conc. of a solution in molality which is obtained by mixing 250 g of 20% solution of NaCl with 200 g of 40% solution of NaCl.

Solution

For 1st solution

100 g of solution contain NaCl = 20 g

250 g of solution contain NaCl = $\frac{20}{100} \times 250$ = 50 g.

For 2nd solution

100 g of solution contain NaCl = 40 g

200 g of solution contain NaCl = $\frac{40}{100} \times 200 = 80$ g.

Hence after mixing

Total mass of NaCl = w = 50 + 80 = 130 g

Formula mass of NaCl = M = 58.5 g/mol

Mass of total solution = 200 + 250 = 450 g.

Mass of Water = W' = 450–130 = 320 g = 0.32 kg

Molality = m = ?

Molality is given by

$$m = \frac{w}{M} \times \frac{1}{W(kg)}$$

$$m = \frac{130}{58.5} \times \frac{1}{0.32} = \boxed{6.94\ m}$$

Q.18 ***(a) An aq. solution of sucrose has been labelled as one molal. Find the mole fraction of solute and the solvent.***

Solution

1 molal aq. sucrose solution means that 1 mole of sucrose (342 g) has been dissolved in 1 kg (1000 g) of H_2O.

Hence

Moles of sucrose = n_{suc} = 1 mole

Mass of H_2O = 1000 g

Mol. Mass of H_2O = 18 g/mol

Moles of H_2O = $n_{H_2O} = \frac{1000}{18} = 55.55$ moles

Therefore

$$x_{suc} = \frac{1}{1+55.55} = 0.0177$$

and $$x_{H_2O} = \frac{55.55}{1+55.55} = \boxed{0.9823}$$

(b) You are provided with 80% sulphuric acid having density 1.8 g/cm³. How much volume of this sulphuric acid sample is required to obtain 1 dm³ of 20% H_2SO_4 whose density is 1.25 g/cm³

Solution

For 80% sulphuric acid

% of sulphuric acid = 80 %

Density of sulphuric acid = 1.8 g/cm³

Thus Mass of 1 cm³ of solution = 1.8 g

Mass of 1000 cm³ of solution = 1.8 x 1000 = 1800 g

Therefore

100 g of solution contain sulphuric acid = 80 g

1800 g of solution contain sulphuric acid = $\frac{80}{100} \times 1800 = 1440$ g.

Hence, 1440 g of H_2SO_4 are present in 1000 cm³ of solution.

Mass of H_2SO_4 / cm³ = w = 1440 g

Molar Mass of H_2SO_4 = M = 98 g/mol

Volume of solution = V = 1000 cm³ = 1 dm³

Therefore, molarity is given by

$$\text{Molarity} = \frac{w}{M} \times \frac{1}{V}$$

$$\text{Molarity} = \frac{1440}{98} \times \frac{1}{1} = 14.7\ M$$

For 20% sulphuric acid

% of sulphuric acid = 20 %

Density of sulphuric acid = 1.25 g/cm³

Thus Mass of 1 cm³ of solution = 1.25 g

Mass of 1000 cm³ of solution = 1.25 x 1000 = 1250 g

Therefore

100 g of solution contain sulphuric acid = 20 g

1250 g of solution contain sulphuric acid = $\frac{20}{100} \times 1250 = 250$ g.

Hence, 250 g of H_2SO_4 are present in 1000 cm³ of solution.

Mass of H_2SO_4 / cm³ = w = 250 g

Mol. Mass of H_2SO_4 = M = 98 g/mol

Volume of solution = V = 1000 cm³ = 1 dm³

Therefore, molarity is given by

$$\text{Molarity} = \frac{w}{M} \times \frac{1}{V}$$

$$\text{Molarity} = \frac{250}{98} \times \frac{1}{1} = 2.55\ M$$

To prepare 1 dm³ (1000 cm³) of 2.55 M H_2SO_4 from 14.7 M H_2SO_4

Conc. H_2SO_4 (given) Dil. H_2SO_4 (required)

$$M_1 V_1 = M_2 V_2$$

or $$V_1 = \frac{M_2}{M_1} \times V_2$$

$$V_1 = \frac{2.55}{14.7} \times 1000 = \boxed{173.47\ cm^3}$$

Therefore 173.47 cm³ of conc. H_2SO_4 are taken in a measuring flask and volume of the solution is made upto 1 dm³ (1000 cm³).

Q.19 ***250 cm^3 of 0.2 molar K_2SO_4 solution is mixed with 250 cm^3 of 0.2 molar KCl solution. Calculate the molar conc. of K^+ ions in the solution.***

Solution:

1 mole of K_2SO_4 produce 2 moles of K^+ ions
Therefore, 0.2 moles of K_2SO_4 produce 0.4 moles of K^+ ions
Hence conc. of K^+ ions = 0.4 moles/dm^3

1 mole of KCl produces 1 moles of K^+ ions
Therefore, 0.2 moles of KCl produces 0.2 moles of K^+ ions
Hence, conc. of K^+ ions = 0.2 moles/dm^3

After mixing two molar solutions
Conc. of K^+ ions = 0.2 + 0.4 = 0.6 moles in 2 dm^3
If 250 cm^3 of each solution is mixed then

$$\text{Total Volume} = 250 + 250 = 500\ cm^3 = \frac{500}{1000} = 0.5\ dm^3$$

Hence 2 dm^3 of solution contain K^+ ions = 0.6 moles

$$0.5\ dm^3 \text{ of solution contain } K^+ \text{ ions} = \frac{0.6 \times 0.5}{2} = 0.15\ \text{moles/dm}^3$$

$$1\ dm^3 \text{ of solution contain } K^+ \text{ ions} = \boxed{0.3\ \text{moles/dm}^3}$$

Q.20 ***5 g of NaCl is dissolved in 1000 g of water. The density of resulting solution is 0.997 g/cm^3. Calculate the molality, molarity and mole fractions of this solution. Assume that the volume of the solution is equal to that of the solvent.***

Molality

Mass of NaCl = w = 5 g
Formula mass of NaCl = M = 58.8 g/mol
Mass of H_2O = W = 1000 g = 1 Kg

$$\text{molality} = \frac{w}{M} \times \frac{1}{W}$$

$$\text{molality} = \frac{5}{58.8} \times \frac{1}{1} = \boxed{0.0854\ m}$$

Molarity

Mass of NaCl = w = 5 g
Formula mass of NaCl = M = 58.8 g/mol
Mass of H_2O = W = 1000 g = 1 Kg

Since volume of solution is equal to the volume of solvent.
And 1 kg of water = 1 dm^3
Therefore volume of solution = V = 1 dm^3

Molarity is given by

$$\text{molarity} = \frac{w}{M} \times \frac{1}{V}$$

$$\text{molarity} = \frac{5}{58.8} \times \frac{1}{1} = \boxed{0.0854\ M}$$

Mole Fraction

Mass of NaCl = w = 5 g
Formula mass of NaCl = M = 58.8 g/mol

$$\text{Moles of NaCl} = \frac{5}{58.5} = 0.0854 \text{ moles}$$

Mass of H_2O = W = 1000 g
Mol. Mass of H_2O = M = 18 g/mol

$$\text{Moles of } H_2O = \frac{1000}{18} = 55.56 \text{ moles}$$

Hence

$$x_{NaCl} = \frac{0.0854}{0.0854 + 55.56} = \boxed{0.00154}$$

$$x_{H_2O} = \frac{55.56}{0.0854 + 55.56} = \boxed{0.9984}$$

Q.21 ***4.675 g of a compound with empirical formula C_3H_3O, was dissolved in 212.5 g of pure benzene. The freezing point of the solution was found 1.02°C less than that of benzene. The molar freezing point constant of benzene is 5.1°C. Calculate***

(i) The relative molar mass of the compound

Mass of solute compound = w_2 = 4.675 g
Mass of solvent benzene = w_1 = 212.5 g
Freezing point depression = ΔT_f = 1.02
Molal F.P. constant of benzene = k_f = 5.1°C
Molecular Mass of compound = M_2 = ?
Molecular Mass of the compound is given by

$$M_2 = \frac{k_f}{\Delta T_f} \times \frac{w_2 \times 1000}{w_1}$$

$$M_2 = \frac{5.1}{1.02} \times \frac{4.675 \times 1000}{212.5} = \boxed{110\ \text{g/mol}}$$

(ii) The molecular formula of the compound

Empirical Formula of the compound $= C_3H_3O$

Empirical formula mass of the compound $= (3 \times 12) + (3 \times 1) + (1 \times 16)$

$= 55\ g\ mol^{-1}$

$$\text{Thus } n = \frac{\text{Molecular Mass}}{\text{Empirical Mass}} = \frac{110}{55} = 2$$

Hence Molecular formula $= n\,(\text{Empirical formula})$

$= 2\,(C_3H_3O)$

$= \boxed{C_6H_6O_2}$

Q.22 The boiling point of a solution containing 0.2 g of a substance 'A' in 20 g of ether is 0.17 K higher than that of pure ether. Calculate the molar mass of 'A'. Boiling point constant of ether is 2.16 K

Solution:

Mass of solute 'A' $= w_2 = 0.2\ g$

Mass of solvent ether $= w_1 = 20\ g$

Elevation in B.P. $= \Delta T_b = 0.17\ K$

Molal B.P. constant of ether $= k_b = 2.16\ K$

Molar Mass of A $= M_2 = ?$

Molar Mass of solute 'A' is given by

$$M_2 = \frac{k_b}{\Delta T_b} \times \frac{w_2 \times 1000}{w_1}$$

$$M_2 = \frac{2.16}{0.17} \times \frac{0.2 \times 1000}{20} = \boxed{127\ g/mol}$$

Q.23 3 g of non-volatile, non-electrolyte solute 'X' is dissolved in 50 g of ether (molar mass 74) at 293 K. The vapour pressure of ether falls from 442 torr to 426 torr at these conditions. Calculate the molecular mass of the solute X.

Solution:

Mass of solute 'X' $= w_2 = 3\ g$

Mass of solvent ether $= w_1 = 50\ g$

Molar Mass of ether $= M_1 = 74\ g/mol$

Vapour pressure of pure ether $= P^o = 442$ torr

Vapour pressure of solution $= P = 426$ torr

Lowering of vapour pressure $= \Delta P = P^o - P = 442 - 426 = 16$ torr

Molar Mass of 'X' $= M_2 = ?$

Molar Mass of solute is given by

$$M_2 = \frac{P^0}{\Delta P} \times \frac{w_2 M_1}{w_1} = \frac{442}{16} \times \frac{3 \times 74}{50} = \boxed{122.6\ g/mol}$$

HELLO! Mr. Question here!

OBJECTIVE: Multiple Choice Questions from PAST PAPERS

1. Which one of the following gives acidic solution when dissolved in H_2O (Rawalpindi 2011)
   (a) NaCl (b) Na_2SO_4 (c) NH_4Cl (d) CH_3COONH_4
2. 0.1 moles of a solute dissolved in 100 g of solvent will be: (Lahore Board, 2009) (Gujranwala board, 2010)
   (a) 0.1 molal (b) 1.0 molal (c) 0.5 molal (d) 0.1 molar
3. The number of moles of solute per kilogram of solvent is called: (Gujranwala board, 2009)
   (a) molality (b) molarity (c) mole-fraction (d) normality
4. The amount of NaOH required to prepare 250 cm^3 of 1 M solution in grams is: (Gujranwala board, 2011)
   (a) 10 (b) 15 (c) 20 (d) 25
5. A thermometer used in Lands Berger's method can read up to (Rawalpindi Board, 2013)
   (a) 0.1 K (b) 0.01 F (c) 0.01 K (d) 0.01o C
6. Which one of the following pair of liquids is not completely miscible? (Multan Board, 2013)
   (a) Alcohol and Water (b) Alcohol and Ether
   (c) Phenol and Water (d) Benzene and Cyclohexane
7. Raoult's Law is represented by: (Lahore Board, 2009)
   (a) $P = P^oX_1$ (b) $\Delta P = P^oX_2$ (c) $\Delta P / P^o = X_2$ (d) all of these
8. Solutions containing relatively lower concentrations of solutes are called: Bahawalpur Board, 2009
   (a) Dilute solution (b) Concentrated solution
   (c) Saturated solutions (d) Ideal solutions
9. The concentration of solute in the solution when it is in equilibrium with the solid substance at a particular temperature is called its. (Sargodha Board, 2009)
   (a) Solubility (b) Molarity (c) Molality (d) Mole fraction
10. 2 g of NaOH is dissolved in 500 cm^3 of solution. The molarity of solutions is (Rawalpindi Board, 2009)
    (a) 2.0M (b) 1.0M (c) 0.2M (d) 0.1M
11. 10g NaOH dissolved per 250 cm^3 of solution has molarity. (Lahore Board, 2010)
    (a) 0.5 M (b) 1.0 M (c) 1.5 M (d) 2.0 M
12. Which is a colligative property? (Faisalabad Board, 2010)
    (a) Change in vapour pressure of a solution.
    (b) change in free energy of a solution.
    (c) Heat of vaporization of solvent in the solution
    (d) Lowering of vapour pressure of a solution.

13. Which one is not equation of Roult's Law (Lahore Board, 2011)

(a) $\Delta P = P^{o}X_2$ (b) $\sqrt{v} = n_2X_2$ (c) $\frac{\Delta P}{P^{o}} = X_2$ (d) $P = P^{o}X_1$

14. Amount of NaOH required to prepare 250 cm^3 of 1 M solution is *(Faisalabad Board, 2011)*

(a) 10 g (b) 6 g (c) 2 g (d) 8 g

15. The number of moles of solute dissolved per dm^3 of solution is called *(D. G. Khan Board 2012)*

(a) Molarity (b) molality (c) Normality (d) mole fraction

16. Benzene-ether can form *(D. G. Khan Board, 2012)*

(a) Ideal solution (b) Non-ideal solution (c) Buffer solution (d) none of these

17. The azeotropic mixture of solution showing posture deviation can be distilled at ________ boiling point *(Faisalabad Board, 2007)*

(a) maximum (b) Minimum (c) No sharp (d) none of these

18. The hydration energy of Br^- ion is ____________ than F- ion *(Faisalabad Board, 2007)*

(a) equal to (b)smaller (c) greater (d) none of these

19. Chemical used to protect a car by preventing the liquid in the radiator from freezing is: *(Faisalabad Board, 2009)*

(a) Phenol (b) Ethylene glycol (c) KNO_3 (d) Methanol

20. Which of the following is an ideal solution: *(D.G. Khan Board, 2010)*

(a) C_2H_5OH and H_2O (b) C_6H_6 and CCl_4

(c) $CHCl_3$ and $(CH_3)_2CO$ (d) H_2O and HCl

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(c)	2	(b)	3	(a)	4	(a)	5	(c)
6	(c)	7	(d)	8	(a)	9	(a)	10	(d)
11	(b)	12	(d)	13	(b)	14	(a)	15	(a)
16	(a)	17	(b)	18	(c)	19	(b)	20	(b)

SHORT & LONG QUESTIONS FROM PAST PAPERS

CONCENTRATION UNITS OF SOLUTIONS

Short Questions

(1) What do you mean by percentage w/w composition of a solution. *(Multan Board, 2008)*
(2) Define molarity. Give one example. *(Multan Board, 2010)*
(3) What is molality. Give its formula? *(Faisalabad Board, 2009: Lahore Board, 2013)*
(4) Define molarity and molality. Give their mathematical expression. *(Lahore Board, 2008, 2014: Multan Board, 2009: Gujranwala Board, 2010: Rawalpindi Board, 2013)*
(5) Define mole fraction and parts per million. *(Sargodha Board, 2010)*
(6) What is (or Define) parts per million (ppm). Give its mathematical expression *(Multan Board, 2007: Lahore Board, 2009: D.G. Khan Board, 2009)* OR Define parts per million and when this concentration unit is used. *(Sargodha Board, 2011)*
(7) How will you prepare 0.2 M NaOH solution? *(D.G. Khan Board, 2009)*
(8) How will you prepare 5% W/V urea solution in water. *(Rawalpindi Board, 2009: Sargodha Board, 2013)*
(9) How will you prepare 10% W/V urea solution in water? *(Faisalabad Board, 2011)*
(10) Calculate the percentage by weight of NaCl if 2g of it is dissolved in 20g of water *(Sargodha Board, 2011: Lahore Board, 2014)*
(11) What is the molality of a solution prepared by dissolving 5g of glucose in 250g of water. *(Sargodha Board, 2013)*
(12) Find the molarity of a solution containing 41.4 g fo K_2CO_3 dissolved in 500cm^3 of given solution. Molar mass of K_2CO_3 is 138 g/mol. *(Multan Board, 2013)*
(13) Calculate the molarity of a solution containing 20.7g of K_2CO_3 dissolved in 500 cm^3 of the given solution. *(D.G. Khan Board, 2011)*

Long Questions

(1) Define the following terms with examples.
(i) Molarity (ii) Molality (iii) Mole fraction (iv) Parts per million *(Sargodha board, 2007: Lahore Board, 2014)*

LIQUID-LIQUID SOLUTIONS, RAOULT'S LAW

Short Questions

(1) What are conjugate solutions? Give examples. *(Lahore Board, 2008)*
(2) What is consulate temperature or critical solution temperature? Give example. *(Multan Board, 2007: D.G. Khan Board, 2010: D.G. Khan Board, 2012: Sargodha Board, 2012, 2013)*
(3) Give two statements of Raoult's law *(Gujranwala Board, 2008: Faisalabad Board, 2008, 2012)* OR What is Raoults law? *(Rawalpindi Board, 2013)*
(4) Cane sugar cannot be dissolved in benzene. Give reason. *(Gujranwala Board, 2014)*
(5) Why glucose is soluble in water but insoluble in CCl_4? *(Sargodha Board, 2007)*

Long Questions

(1) State one form of Raoult's law. *(Bahawalpur Board, 2010)* (2) (as a part of question)
(2) State different forms of Raoult's Law. *(Lahore Board, 2011)* OR What is Raoult's law? Give its three statements. How this law can help us to understand the ideality of a solution. *(D.G. Khan Board, 2012)* OR Give three statements of Raoult's law and also mention how

Raoult's law helps in determining the ideality of a solution. (Gujranwala Board, 2008; Lahore Board, 2013; Rawalpindi Board, 2014)
(3) Define Raoult's law and derive the equation $\Delta P = P^{\circ} X_2$ (Sargodha Board, 2014)
(4) What is Raoult's law? Explain when both components are volatile. (Multan Board, 2010)
(5) Discuss Roults Law for the solution in which both component are volatile. (Sargodha Board, 2011; Faisalabad Board, 2013)

IDEAL AND NON-IDEAL SOLUTIONS

Short Questions

(1) Give any two points which show the ideality of a solution. (Lahore Board, 2008)
(2) Give two pairs of liquids which form ideal solution. (D.G. Khan Board, 2012)
(3) Differentiate between ideal and non-ideal solutions. (Bahawalpur Board, 2009; Rawalpindi Board, 2011; Lahore Board, 2013)
(4) Non-ideal solutions do not obey Raoult's law. Explain (Sargodha Board, 2009; D.G. Khan Board, 2009; Rawalpindi Board, 2010)
(5) Many solutions do not behave ideally. Give reason. (Gujranwala Board, 2014)

Long Questions

(1) Explain the difference between ideal and non ideal solution. (Sargodha Board, 2010; Bahawalpur Board, 2012) OR Distinguish between ideal and non-ideal solution. (Bahawalpur Board, 2010) (2) (as a part)

ZEOTROPIC AND AZEOTROPIC MIXTURES, DEVIATIONS FROM RAOULT'S LAW

Short Questions

(1) Define Zeotropic mixtures. Give one example. (Lahore Board, 2014)
(2) What is positive deviation from Raoult's law? (Lahore Board, 2007)
(3) Differentiate between zeotropic and azeotropic mixtures. (Multan Board, 2011)

Long Questions

(1) What are non-ideal solutions (or azeotropes)? Discuss their types with example. (Faisalabad Board, 2007; Gujranwala Board, 2013)
(2) Define non-ideal solutions and explain positive deviation with the help of a graph. (Sargodha Board, 2013)
(3) Explain negative deviations from Raoult's law. (D.G. Khan Board, 2011)
(4) What are ideal solutions? Graphically explain that how the ideal solutions of two liquids can be separated by fractional distillation. (D.G. Khan Board, 2009)
(5) What are ideal solutions? Explain the fractional distillation of ideal mixture of two liquids. (Lahore Board, 2012)
(6) Explain the fractional distillation. Justify the two curves when composition is plotted against boiling point of the solution. (Faisalabad Board, 2012)

SOLUBILITY, SOLUBILITY CURVES, FRACTIONAL CRYSTALLIZATION

Short Questions

(1) Define solubility curve. Name its two types. (Faisalabad Board, 2012)
(2) Why some substances show discontinuous curves? (D.G. Khan Board, 2008)
(3) Differentiate between continuous and discontinuous solubility curves. (Lahore Board, 2011)

(4) Why fractional crystallization is carried out? (Rawalpindi Board, 2010; Bahawalpur Board, 2011) OR Define fractional crystallization. How it is useful? (D.G. Khan Board, 2011)

Long Questions

(1) Define solubility curves and gives its types with suitable examples. (Faisalabad Board, 2009)
(2) Define solubility and make clear difference between continuous and discontinuous solubility curves. (Faisalabad Board, 2010; Gujranwala Board, 2011)

COLLIGATIVE PROPERTIES

Short Questions

(1) Define colligative properties. Name some important colligative properties. (D.G. Khan Board, 2010; Lahore Board, 2011; Faisalabad Board, 2013; Sargodha Board, 2014)
(2) Define ebullioscopic constant (or molal elevation constant or molal boiling point constant) with one example. (Lahore Board, 2012)
(3) What is molal freezing point constant (or cyroscopic constant) (Bahawalpur Board, 2008) OR What is cryoscopic constant. Give its value of water. (Sargodha Board, 2007)
(4) State Ebullioscopic constant and Cryoscopic constant. (Multan Board, 2011)
(5) Give the conditions of colligative properties. (Sargodha Board, 2011)
(6) What are colligative properties? Classify these and explain any one. (Rawalpindi Board, 2009)

LOWERING OF VAPOUR PRESSURE, ELEVATION OF BOILING POINT, DEPRESSION OF FREEZING POINT, APPLICATIONS OF COLLIGATIVE PROPERTIES

Short Questions

(1) Why is the vapour pressure of a solution less than pure solvent? (Lahore Board, 2014)
(2) Lowering of vapour pressure is colligative property. Explain. (Gujranwala Board, 2014)
(3) Depression in freezing point is a colligative property. Justify. (Lahore Board, 2013)
(4) Give two applications of colligative properties. (Sargodha Board, 2013)
(5) Ethylene glycol may be used in radiator of an automobile. Give two aspects of its use (Multan Board, 2008; Gujranwala Board, 2013)

Long Questions

(1) Define colligative properties. Describe the lowering of vapour pressure in terms of colligative property of solution and derive the expression for molecular mass of non-volatile solute. (Bahawalpur Board, 2009)
(2) Give graphical explanation for elevation of boiling point of a solution. (Lahore Board, 2009) OR Define OR Explain elevation of boling point with the help of figure. (Lahore Board, 2010) OR Explain colligative properties. Explain elevation of boiling point. (Faisalabad Board, 2011) OR Explain elevation of boiling point of a solvent by solute with the help of a graph. Derive formula for determination of molecular mass of an unknown solute from this concept. (D.G. Khan Board, 2007) OR Explain Elevation of Boiling Point with the help of figure: (Multan Board, 2009, 2011, 2012; Bahawalpur Board, 2011; Gujranwala Board, 2010)
(3) What is boiling point elevation. Describe a method to determine the boiling point elevation of a solution. (Sargodha Board, 2009) OR What is the elevation of boiling point and how it can be measured by Landberger's method? (Rawalpindi board, 2007; Gujranwala Board, 2012; Sargodha Board, 2012) OR Define and classify colligative properties. How

boiling point elevation is measured by Landberger's Method? (Lahore Board, 2007)

(4) Describe the freezing point depression method for the determination of molecular ma of an organic compound. (Lahore Board, 2014)

(5) Define freezing point. Write down the measurement of freezing point depression b Beckmann's freezing point apparatus. (Gujranwala Board, 2009, 2014)

HYDRATION AND HYDROLYSIS

Short Questions

(1) What are hydrates? How are they formed? Give examples. (Lahore Board, 2007: Bahawalpur Board, 2008: Rawalpindi Board, 2010: D.G. Khan Board, 2012: Multan Board, 2010: Faisalabad Board 2013)

(2) What is meant by water of crystallization? Give two examples. (Lahore Board, 2010, 2014)

(3) Define hydrolysis and give its two examples. (Rawalpindi Board, 2010: Gujranwala Board, 2013)

(4) Differentiate between hydration and hydrolysis with one example each. (Lahore Board 2008: Sargodha Board, 2010: Multan Board, 2012)

(5) Why aqueous solution of NH_4Cl is acidic but CH_3COONa is basic? (Gujranwala Board, 2008)

(6) Dissolution of KCl and Na_2SO_4 in water give neutral solutions. Why? (Lahore Board, 2011)

(7) The solution of Na_2CO_3 in water is basic in nature. (D.G. Khan Board, 2008)

(8) Aqueous solution of $CuSO_4$ is acidic, whereas aqueous solution of CH_3COONa is basic Justify? (Bahawalpur Board, 2009: Gujranwala Board, 2015)

(9) How the solution of $CuSO_4$ is acidic in nature? (Multan Board, 2007: Sargodha Board, 2008: Lahore Board, 2012) OR Explain why $CuSO_4$ give acidic solution when put in water? (D.G. Khan Board, 2010)

(10) Aqueous solution of ammonium chloride is acidic in nature. Justify (Azad Kashmir Board, 2012)

Long Questions

(1) Explain hydrolysis reaction with two examples. (Rawalpindi Board, 2010) OR Define hydrolysis. Why the aqueous solution of NH_4Cl is acidic and that of CH_3COONa is basic (Sargodha Board, 2013)

(2) Differentiate between hydration and hydrolysis with the help of suitable examples (D.G. Khan Board, 2010)

(3) Write not on hydration reaction. (D.G. Khan Board, 2012)

(4) Differentiate between hydration and hydrolysis with suitable examples. (Azad Kashmir Board 2012)

TEST YOUR SKILLS

Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) Azeotropic mixtures are
(a) constant boiling mixture (b) those which boil at different temperature
(c) mixture of two solids (d) none of the above

(ii) Which is not a colligative property?
(a) freezing point (b) lowering of vapour pressure
(c) depression of freezing point (d) elevation of boiling point

(iii) Colligative properties of the solution depend upon
(a) nature of solute (b) number of solute particles
(c) nature of solvent (d) number of moles of solvent only

(iv) If 18g of glucose ($C_6H_{12}O_6$) is present in 1000 g of an aqueous solution of glucose, it is said to be
(a) 1 molal (b) 1.1 molal (c) 0.5 molal (d) .01 molal

(v) Solution which distils without change in composition is called
(a) amorphous (b) azeotropic solution (c) ideal (d) supersaturated

(vi) In a mixture of 28 grams of N_2 and 96 grams of O_2 the mole fraction of N_2 is
(a) 1.1 (b) 0.51 (c) 0.25 (d) 0.11

(vii) A molal solution is one that contains one mole of a solute in
(a) 1000 g of the solvent (b) one dm^3 of the solvent
(c) one dm^3 of the solution (d) 22.4 dm^3 of the solution

(viii) The law of the relative lowering of vapour pressure was given by
(a) Raoult (b) Ostwald (c) Vant Hoff (d) Lewis

(ix) The number of moles in 180 g of water is
(a) 1 (b) 10 (c) 18 (d) 100

(x) Formula mass of NaCl is 58.5. A solution of NaCl containing 5.85 g NaCl per dm^3 is
(a) 1 molar (b) 0.1 molar (c) 2 molar (d) 0.585 molar

(xi) The molarity of glucose solution is 0.04. the mass of glucose in 250 cm^3 of the solution is
(a) 1.8 g (b) 0.18 g (c) 1.18 g (d) 18 g

(xii) Cane sugar is soluble in water but insoluble in benzene because
(a) cane sugar is a non-polar molecule (b) cane sugar is an ionic compound
(c) cane sugar has hydrogen bonding (d) can sugar is an organic compound

(xiii) When equal volumes of ether and water are shaken, then two layers are formed. The ether layer contains water
(a) 2.1 % (b) 1.2% (c) 5.6% (d) 6.5%

(xiv) Vapour pressure of pure water is 28.4 torr. Cane sugar is dissolved in it and the vapour pressure of solution becomes 25 torr. The mole fraction of cane sugar is
(a) 0.48 (b) 0.24 (c) 0.12 (d) 0.02

(xv) Increase in temperature increases the solubility of a salt except
(a) $K_2Cr_2O_7$ (b) $Pb(NO_3)_2$ (c) KNO_3 (d) $Ce_2(SO_4)_3$

(xvi) Which one of the following is used as antifreeze in the radiator?
(a) sodium chloride (b) water (c) ethylene glycol (d) glycerine

(xvii) Which salt dissolved in water forms a solution with a pH greater than 7.
(a) NaCl (b) $CuSO_4$ (c) Na_2CO_3 (d) NH_4Cl

SUBJECTIVE

Time: 2:10 Hours **Marks: 68**

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question numbers carefully. (22x 2)=44

Section - I

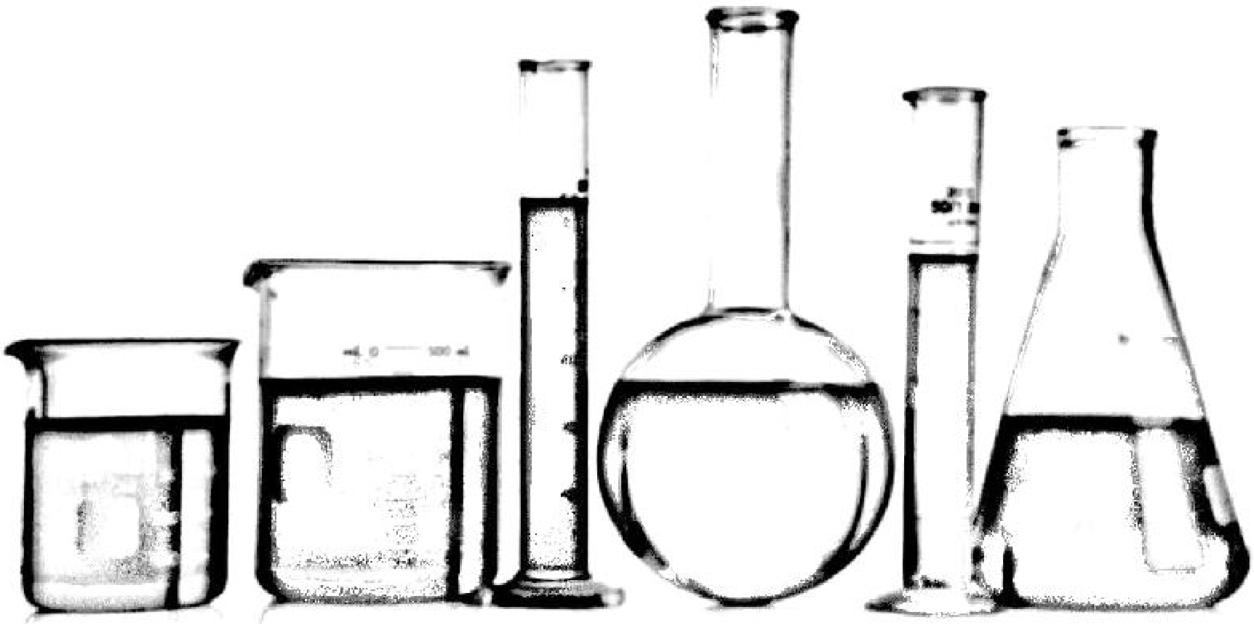
Q2. Answer any Eight parts from the following.

(i) How many grams of sugar will be dissolved to make 1.5 dm3 of sugar solution?

COLLEGE CHEMISTRY

Intermediate Part I

11



DR. JAMSHED AKBAR

Muhammad Munir

Tallat Jamshed | Shahid Ali | Prof. Dr. Rana Taj

Zaheer Abdullah | M. Ashraf Kamal | M. Mazhar Iqbal Qureshi

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(ii) What are mole fraction and mole percentage?
(iii) Can sugar is not soluble in petrol and benzene but it dissolves in water. Why?
(iv) Lattice energy of ionic solids is always higher than molecular solids. Why?
(v) How can it be predicted that process of dissolution will be endothermic or exothermic?
(vi) Define ebullioscopic and cryoscopic constants?
(vii) Why discontinuous solubility curves are formed?
(viii) What is the role of antifreeze in radiator of an automobile?
(ix) How can you calculate the molecular mass of a solute by cryoscopic method?
(x) When a non-volatile solute is dissolved in volatile solvent, vapour pressure of solvent is lowered. Explain why?
(xi) Differentiate between ideal and non-ideal solutions
(xii) Define water of crystallization with examples

Q3. Answer any Eight parts from the followings.
(i) Calculate percentage by weight of NaCl when 2 g of NaCl is dissolved in 20 g of water?
(ii) A solution contain 8.4 g of $NaHCO_3$ in 1 dm^3 of the solution. Calculate its molarity?
(iii) Molality of solution is not changed but molarity is changed by change in temperature. Why?
(iv) A solution contains 18 g glucose, 4.6 g urea and 1.8 g of water. Calculate mole fraction of each component?
(v) Define Mole Fraction and parts per million and when these units are used?
(vi) Give two examples of solution of solid in solid?
(vii) Cane sugar is insoluble in petrol but soluble in water. Why?
(viii) What are conjugate solutions?
(ix) What is consulate temperature?
(x) When phenol and water are mixed together in equal volume to form two layers then what is the effect of temperature on this system?
(xi) Why some properties are called colligative?
(xii) Make difference between Hydration and Hydrolysis?

Q4. Answer any Six parts from the followings.
(i) Differentiate between ideal and non-ideal solutions?
(ii) Why a solution of benzene and toluene is an ideal solution?
(iii) What are zeotropic mixtures?
(iv) What is the maximum boiling point azeotrope. Give example?
(v) What is fractional crystallization?
(vi) What conditions are necessary for normal colligative properties?
(vii) Which thermometer is used in landsberger's method for measuring elevation of boiling point and why?
(viii) How can a freezing mixture be prepared?
(ix) Aqueous solution of NH_4Cl and $CuSO_4$ are acidic. Why?

Section - II (Attempt any three questions). (8 X 3) = 24

Q5. (a) Discuss Raoult's law for the solution in which both components are volatile. (04)
(b) Define elevation in boiling point. Explain this with the help of graph. (04)

Q6. (a) Define the following terms. (04)
(i) % w/w (ii) ppm (iii) molality (iv) zeotropic mixture
(b) The boiling point of a solution containing 0.2 g of a substance 'A' in 20 g of ether is 0.17 K higher than that of pure ether. Calculate the molar mass of 'A'. Boiling point constant of ether is 2.16 K (04)

Q7. (a) Discuss the measurement of mass of solute by Beckmann's method. (04)
(b) What are partially miscible liquids? Describe phenol-water system (02)

Q8. (a) Differentiate between hydration and hydrolysis. (03)
(b) Explain why?
(i) Aqueous solution of $Al_2(SO_4)_3$ is acidic. (ii) Aqueous solution of Na_2CO_3 is alkaline (03)
(b) What is hydration energy? On what factors does it depend? Give example (04)

Q9. (a) What are colligative properties. Why are these called colligative? Explain
(b) You are provided with 80% sulphuric acid having density 1.8 g cm^{-3}. How much volume of this sulphuric acid sample is required to obtain 1 dm^3 of 20% H_2SO_4 whose density is 1.25 g/cm^3 (04)

Chapter 10

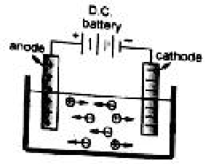
ELECTROCHEMISTRY

Galvani

Modern Batteries

CONTENTS

Chapter-10 Electrochemistry



INTRODUCTION

Electrochemistry

The branch of chemistry, which deals with the conversion of electrical energy into chemical energy and chemical energy into electrical energy, is called electrochemistry.

Oxidation

It may be defined as the addition of oxygen, loss of hydrogen or loss of electrons from a species.

Reduction

It may be defined as the removal of oxygen, addition of hydrogen or addition of electrons from a species.

Oxidation Reaction

A reaction in which a substance loses electrons is called oxidation reaction.

e.g., $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$

Reduction Reaction

The reaction in which a substance gains electrons is called reduction reaction.

e.g., $Cu^{+2}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

- Oxidation – reduction reactions are also known as redox reactions.
- In a redox reaction, oxidation number of elements undergoes changes.

OXIDATION STATE AND BALANCING OF REDOX EQUATIONS

OXIDATION NUMBER OR OXIDATION STATE

It is the apparent charge on an atom of an element in a molecule or an ion.

It may be positive or negative or zero.

Examples:

- The oxidation state of free H_2 is zero
- The oxidation state of Na and Cl are +1 and −1 respectively.

Rules for Assigning Oxidation Numbers

1. The oxidation number of a free element is zero. e.g. H_2^0, Na^0, Mg^0.
2. The oxidation number of hydrogen is +1, except in the case of metal hydrides e.g. NaH, MgH_2 where it is −1.
3. The oxidation number of oxygen is −2, except in the case of metal peroxides, where it is −1, in superoxides, where it is −½ and in OF_2, where it is +2.
4. In binary compounds, the oxidation numbers of group VII A halogens is −1.
5. The oxidation number of each element of the groups I-A, II-A and III-A are +1, +2 and +3 respectively.
6. In a neutral compound, the sum of oxidation numbers of all the atoms is equal to zero.
7. The oxidation number of an ion consisting of single element is the same as the charge on the ion. e.g. oxidation states of K^+, Ca^{2+}, Al^{3+}, Br^-, S^{2-} are +1, +2, +3, 1 and -2 respectively.
8. In ions, the sum of oxidation numbers of all the atoms is equal to the charge on the ion.
9. In any substance, the more electronegative element has the negative oxidation number.

Example 1

- Determine the oxidation number (O.N.) of Mn in $KMnO_4$

(D.G. Khan Board, 2007; Multan Board, 2010; D.G. Khan Board, 2011; Rawalpindi Board, 2012 Sargodha Board, K13 Lahore Board, 2013, 2014)

Oxidation number of K $= +1$

Oxidation number of O $= -2$

Let oxidation number of Mn $= x$

Thus for $KMnO_4$

$$+1 + x + 4(-2) = 0$$

$$x - 7 = 0$$

or $$x = +7$$

Example 2

- Determine the oxidation number (O.N) of N in NH_4^+

Oxidation number of H = +1

Let oxidation number of N = x

Thus for NH_4^+,

$$x + 4(+1) = +1$$

$$x + 4 = +1$$

$$x = 1 - 4$$

Or $$x = -3$$

BALANCING OF EQUATIONS BY OXIDATION NUMBER METHOD

This method is based on the principle that

The total number of electrons lost by a reducing agent is equal to the total number of electrons gained by an oxidizing agent.

Following rules are used for balancing equation by oxidation number method.

1. Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.
2. Indicate the number of electrons gained or lost by means of arrows.
3. Equate the number of electrons gained and lost by multiplying them with suitable numbers.
4. Use the suitable numbers obtained in step (iii), to balance the principle reactants and products.
5. Balance the rest of equation by inspection method.

Example:

$$Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$$

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$\overset{0}{Cu} + H\overset{+5}{N}O_3 \longrightarrow \overset{+2}{Cu}(\overset{+5}{N}O_3)_2 + \overset{+2}{N}\overset{-2}{O} + H_2O$$

- In this equation N is reduced from +5 in HNO_3 to +2 in NO. But it's oxidation state is not changed in $Cu(NO_3)_2$. Therefore, write HNO_3 twice and determine the number of electrons gained and lost and equate them.

gain of $3e^- \times 2 = 6e^-$

$$\overset{0}{Cu}, \quad H\overset{+5}{N}O_3, \quad \overset{+2}{Cu}(NO_3)_2, \quad \overset{+2}{N}O$$

$$HNO_3 + Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$$

loss of $2e^- \times 3 = 6e^-$

- Use the numbers obtained in above step to balance Cu and HNO_3.

  Thus, Cu is multiplied by 3 and HNO_3 by 2.

  $$HNO_3 + 3Cu + 2HNO_3 \longrightarrow Cu(NO_3)_2 + NO + H_2O$$

- Balance the rest of equation by inspection method.

  $$6HNO_3 + 3Cu + 2HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

  or $$3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

BALANCING OF EQUATIONS BY ION ELECTRON METHOD

It is based on the principle that

The total number of electrons lost by a reducing agent is equal to the total no. of electrons gained by an oxidizing agent.

Following rules are used for balancing equation by ion electron method.

1. Write skeleton equation showing only those substances, which are actually involved in the reaction.
2. Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.
3. If element undergoing oxidation state is free then it is written as such, otherwise it should be written as molecular or ionic specie.
4. Balance each half reaction separately.
5. Balance oxygen by adding H_2O.
6. Balance hydrogen by adding H^+ ions in case of acidic media and OH^- ions in case of basic media.
7. Write down the number of electrons gained and lost in each half reaction
8. Equate the total number of electrons gained and lost by multiplying the two half reactions by suitable numbers.
9. Finally, add the two half reactions to get the resultant balanced equation.
10. Simplify the resultant equation if necessary, in order to obtain the net ionic equation.

Example 1 (Acidic media):

$$Cl^- + MnO_4^- \longrightarrow Cl_2 + Mn^{2+}$$

(D.G. Khan Board, 2009)

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

  $MnO_4^- \longrightarrow Mn^{2+}$ (reduction half reaction)

  $2Cl^- \longrightarrow Cl_2$ (oxidation half reaction)

- Balance oxygen by adding H_2O.

  $MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

  $2Cl^- \longrightarrow Cl_2$

- Balance hydrogen in each half reaction by adding H^+ ions.

  $8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$

  $2Cl^- \longrightarrow Cl_2 + 2e^-$

- Write down the number of electrons gained and lost in each half reaction.

  $8H^+ + MnO_4^- + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ ____ (1)

  $2Cl^- \longrightarrow Cl_2 + 2e^-$ ____ (2)

- Equate the total number of electrons gained and lost by multiplying eq.(1) by 2 and eq.(2) by 5.

  $16H^+ + 2MnO_4^- + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$

  $10Cl^- \longrightarrow 5Cl_2 + 10e^-$

- Finally, add the two half reactions to get the resultant balanced equation.

  $16H^+ + 2MnO_4^- + 10e^- \longrightarrow 2Mn^{2+} + 8H_2O$

  $10Cl^- \longrightarrow 5Cl_2 + 10e^-$

  $$2MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 5Cl_2 + 8H_2O$$

To write electrons lost or gained, following formula is used
Total charge on L.H.S. – Total charge on R.H.S.
If the answer is negative, then the electrons are lost. Therefore, add electrons on R.H.S.
If the answer is positive, then the electrons are gained. Therefore, add electrons on L.H.S.
e.g. In the above example
For reduction half reaction, (+8 – 1) – (+2) = +5, Thus, add $5e^-$ on L.H.S.
For oxidation half reaction, (– 2) – (0) = – 2, Thus, add $2e^-$ on R.H.S.

Example 2 (Basic Media):

$$MnO_4^- + C_2O_4^{2-} + H_2O \longrightarrow MnO_2 + CO_2 + OH^-$$

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$$MnO_4^- \longrightarrow MnO_2 \quad \text{(reduction half reaction)}$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 \quad \text{(oxidation half reaction)}$$

- Balance hydrogen and oxygen by adding H_2O and OH^- ions.

$$2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^- \quad \_\_\_\_ (1)$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 \quad \_\_\_\_ (2)$$

- Write down the number of electrons gained and lost in each half reaction

$$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^- \quad \_\_\_\_ (1)$$
$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \quad \_\_\_\_ (2)$$

- Equate the total number of electrons gained and lost by multiplying eq.(2) by 3 and eq.(1) by 2, and then add the two half reactions.

$$6e^- + 4H_2O + 2MnO_4^- \longrightarrow 2MnO_2 + 8OH^- \quad \_\_\_\_ (1)$$
$$3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^- \quad \_\_\_\_ (2)$$

$$3C_2O_4^{2-} + 4H_2O + 2MnO_4^- \longrightarrow 2MnO_2 + 8OH^- + 6CO_2$$

ELECTRICAL CONDUCTION

Electrical Conduction

Flow of electric current through a medium is called electrical conduction

It may be of two types

(1) Electrolytic Conduction

The conduction of electricity carried out by ions present in fused or in an aqueous solution of an electrolyte is called electrolytic conduction.

e.g. The molten or aqueous solution of NaCl contain Na^+ and Cl^{-1} ions. These ions conduct electricity.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$

(2) Metallic Conduction

The conduction of electricity through a metal due to free electrons is called metallic conduction.

All metals are good conductors of electricity.

Electrolysis

The process is which electricity is used to carry out a non-spontaneous process.

This process is done in an electrolytic cell.

Example:

The sodium metal is manufactured on industrial scale in Down's cell by the electrolysis of molten NaCl.

$$2NaCl \xrightleftharpoons{Electricity} 2Na + Cl_2$$

Ionization

The process in which ionic compounds when fused or dissolved in water split up into charged particles called ions.

e.g.

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^-$$

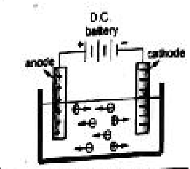
ELECTROCHEMICAL CELLS

These are of two types

1. Electrolytic Cells
2. Voltaic or Galvanic Cells

Electrolytic Cells

The cell in which electric current is used to carry out a non-spontaneous reaction is called electrolytic cell. The process is called electrolysis.



Examples:

Down's cell, Nelson's cell

Construction

- It consists of two electrodes dipped into a solution of an electrolyte, containing positive and negative ions, which can move freely in the solution.
- Positive electrode is called anode and negative electrode is called cathode.
- Electrodes can be connected to a direct current (D.C.) source, for electrical supply.

Working

- When electrodes are connected to a D.C. source electric potential is produced. The potential moves the positive ions towards negative electrode (cathode) and negative ions towards positive electrode (anode). Thus electrolytic conduction occurs in electrolytic cell.
- The movement of ionic charges through the liquid brought by the application of electricity is called electrolytic conduction and the apparatus used is called electrolytic cell.
- When ions reach the electrodes, electrochemical reactions occur.
  At anode, negative ions give up electrons. This process is called oxidation
  At cathode, positive ions take up electrons. This process is called reduction.
- Hence, an oxidation–reduction reaction starts in the cell and various products are obtained. The electrons flow through external wire. The electrons flow from anode to cathode.
- The solution will continue conducting electricity until this redox reaction is taking place in the cell.

> The electrochemical reactions that occur at the electrodes during the electrolytic conduction constitute the phenomenon of electrolysis.

Products

For molten slats, products can be predicted. But in aqeous solution, it is difficult to predict product.

Further electrodes may or may not involve in reaction

Following are some products produced from electrolytes.

- *When electrodes are inert (Pt or Graphite)*

Electrolyte	At Cathode	At Anode
$PbBr_{2(l)}$	$Pb_{(s)}$	$Br_{2(g)}$
$NaCl_{(l)}$	$Na_{(s)}$	$Cl_{2(g)}$
$NaCl_{(aq)}$	$H_{2(g)}$	$Cl_{2(g)}$
$CuCl_{2(aq)}$	$Cu_{(s)}$	$Cl_{2(g)}$
$CuSO_{4(aq)}$	$Cu_{(s)}$	$O_{2(g)}$
$NaOH_{(aq)}$	$H_{2(g)}$	$O_{2(g)}$
$H_2SO_{4(aq)}$	$H_{2(g)}$	$O_{2(g)}$
$KNO_{3(aq)}$	$H_{2(g)}$	$O_{2(g)}$

- *When electrodes take part in reaction*

Electrolyte	Cu Cathode	Cu Anode
$CuSO_{4(aq)}$	Cu deposits	$Cu_{(s)}$ dissolves to form Cu^{2+} ions
Electrolyte	Ag cathode	Ag anode
$AgNO_{3(aq)}$ and $HNO_{3(aq)}$	Ag deposits	$Ag_{(s)}$ dissolves to form Ag^{+} ions

EXPLANATION OF ELECTROLYSIS

Electrolysis of Fused salts

- When a fused salt of an electrolyte is electrolysed, cations reach the cathode where they take up electrons and become discharged, while
- Anions move towards anode, where they give up electrons and become discharged.

Example

$$PbCl_2 \xrightleftharpoons{\text{fused}} \underset{\text{(to cathode)}}{Pb^{2+}} + \underset{\text{(to anode)}}{2Cl^{-1}}$$

At cathode (Reduction)

$$Pb^{2+} + 2e^- \longrightarrow Pb_{(s)}$$

At Anode (oxidation)

$$2Cl^- \longrightarrow Cl_{2(g)} + 2e^-$$

Overall Reaction

$$PbCl_2 \longrightarrow Pb_{(s)} + Cl_{2(g)}$$

- Similarly fused NaCl and $PbBr_2$ are decomposed during electrolysis. Fused Pb and Na are collected at cathode and $Cl_{2(g)}$ and $Br_{2(g)}$ are collected at anode respectively.

NOTE

- Electrons flow from anode to cathode.
- Electric current is conducted in the electrolyte by ions.
- Electric current is conducted through the external circuit by electrons.

Electrolysis of Aqueous Solution of Salts

When an aqueous solution of salt is electrolysed, products are not easily predictable. It is because H_2O can be both oxidised and reduced and some metal cations are not discharged from their aqueous solution.

Example: Electrolysis of Aqueous $NaNO_3$

Consider the electrolysis of an aqueous solution of $NaNO_3$.

$NaNO_3$ ionizes as

$$NaNO_3 \rightleftharpoons Na^+ + NO_3^-$$

In $NaNO_3$ solution, small amount of hydronium ions (H_3O^+) and hydroxyl ion (OH^-) is present due to little ionization of water.

i.e. $$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+ + OH^-$$

Reaction at cathode (Reduction)

When aqueous $NaNO_3$ is electrolyzed, Na^+ ions are not discharged at cathode. Instead H_3O^+ ions take up electrons to form hydrogen atoms.

$$H_3O^+ + e^- \longrightarrow H_{(g)} + H_2O$$

$H_{(g)}$ atoms then combine to form hydrogen gas.

$$H_{(g)} + H_{(g)} \longrightarrow H_{2(g)}$$

Thus, H_2 gas is liberated at cathode

Although very less 10^{-7} mol/ dm^3 of H_3O^+ ions are present in solution. But as soon as H_3O^+ is discharged, new H_3O^+ ions are produced in solution and thus process continuous.

Na^+ ions remain in solution. It is called spectator ion.

Reaction at anode (Oxidation)

At anode, both OH^- and NO_3^{-1} will be present. However, OH^- ions are easily discharged.

$$OH^- \longrightarrow OH_{(aq)} + e^-$$

$OH_{(aq)}$ then give following reaction

$$4OH_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)}$$

Hence, O_2 is produced at anode. While NO_3^- ion is spectator ion.

Order of discharge of ions may also depend upon their concentration.

Overall Reaction

Overall reaction including all the spectator ions.

$$Na^+_{(aq)} + NO_3^-{}_{(aq)} + 2H_2O_{(l)} \longrightarrow Na^+_{(aq)} + NO_3^-{}_{(aq)} + O_{2(g)} + 2H_{2(g)}$$

Electrolytic Processes of Industrial Importance

Exercise Q7.

Describe the electrolysis of molten sodium chloride, and a concentrated solution of sodium chloride. ***(Write Down's Cell and Nelson's Cell)***

1. *Manufacture of Sodium (Down's Cell)*

Na is produced in Down's cell commercially by the electrolysis of fused NaCl between iron cathode and graphite anode. Cl_2 is obtained as by product.

$$NaCl \rightleftharpoons Na^+_{(l)} + Cl^-_{(l)}$$

At Anode (Oxidation)

$$2Cl^-_{(l)} \longrightarrow Cl_{2(g)} + 2e^-$$

At Cathode (Reduction)

$$2Na^+_{(l)} + 2e^- \longrightarrow 2Na_{(s)}$$

Net Reaction

$$2Na^+ + 2Cl^- \longrightarrow 2Na + Cl_2$$

2. *Manufacture of NaOH (Nelson's Cell etc.)*

Caustic soda is produced by electrolysis of an aq. solution of NaCl between Titanium anode and Hg or Ag cathode. The process is carried out in Nelson's cell or Castner – Kellner cell or Hg – cell.

$$2NaCl \underset{}{\overset{H2O}{\rightleftharpoons}} 2Na^+_{(aq)} + 2Cl^-_{(aq)}$$

At Anode (Oxidation)

$$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$$

At Cathode (Reduction)

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$$

Net Reaction

$$2Na^+_{(aq)} + 2Cl^-_{(aq)} + 2H_2O_{(l)} \longrightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)} + Cl_{2(g)}$$

Here Cl_2 and H_2 are obtained as by product.

Na^+ is not discharged at cathode.

3. *Manufacture of Mg and Ca*

Mg and Ca metals are extracted by the electrolysis of their fused chlorides. Mg and Ca are collected at cathode and Cl_2 at anode.

4. *Manufacture of Aluminium*

Al is extracted by the electrolysis of fused Bauxite ($Al_2O_3 . 2H_2O$) in the presence of fused cryolite (Na_3AlF_6). This process is called Hall–Heroult process.

5. Manufacture of Anodized Aluminium

Anodized Al is prepared by making it an anode in an electrolytic cell containing sulphuric acid or chromic acid. A thin layer of oxide is coated over Al. This layer resists corrosion. The freshly anodized Al is hydrated and can absorb dyes.

6. Refining of Copper

Cu is made pure in an electrolytic cell in which impure Cu is made anode and a thin sheet of pure Cu is made Cathode. $CuSO_4$ is used as electrolyte.

The atoms of Cu from impure Cu anode are converted to Cu^{2+} ions and goes into the solution. From solution Cu^{2+} ions are reduced to Cu metal and deposit on cathode. The cathode is made up of pure copper. The impurities are left with anode.

7. Electroplating

Copper, Silver, Nickel or Chromium plating is done by various types of electrolytic cells. In the process, one metal is deposited at the surface of other metal.

Exercise Q13.
Describe a galvanic cell explaining the function of electrodes and salt bridge.

VOLTAIC OR GALVANIC CELL (Zn – Cu Cell)

The cell in which a spontaneous redox reaction is used to produce electric current is called Voltaic or Galvanic cell.

Example

Daniel's cell, Ni–Cd cell, Fuel cell

Consider Zn–Cu cell

Construction

It consists of two half cells that are electrically connected. In each half cell, half reaction takes place. Overall reaction of the cell is the sum of two half cell reactions.

In each half cell, an electrode is dipped into solution of its ions. Zn electrode is dipped in $ZnSO_4$ solution while Cu is dipped in $CuSO_4$ solution.

Two electrodes are connected by wire, while two solutions are connected by salt bridge.

Salt bridge consists of an aqueous solution of KCl in gel.

Working

Cu electrode is dipped in 1M $CuSO_4$ solution in one half cell giving following equilibrium

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$$

Zn electrode is dipped in 1M $ZnSO_4$ solution in other half cell giving following equilibrium

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$$

Two half cells are electrically connected by a salt bridge.

When two electrodes are connected by a wire, electrons start flowing from Zn electrode to Cu electrode.

It is because Zn has greater tendency to give electron than Cu. Thus it becomes more negative than Cu.

Reactions of Zn-Cu galvanic cell

At anode (oxidation)

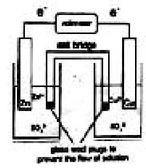
$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

At cathode (reduction)

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

Overall reaction

$$Cu^{2+}_{(aq)} + Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \quad E^\circ = 1.1\ V$$



This Voltaic cell can be represented as

$Zn_{(s)}/Zn^{2+}_{(aq)}(1M)\,||\,Cu^{2+}_{(aq)}(1M)/Cu_{(s)}$ $E^\circ = 1.1\ V$

Function of Salt Bridge

A Salt bridge consists of an aqueous solution of KCl in gel. It performs following functions

- It brings electrical contact between two half–cells.
- It helps to separate the two solutions of half cells. If solutions were mixed, direct chemical reaction would occur and half cells would be destroyed.
- It maintains electrical neutrality of two solutions.

During reaction, Zn half cell continuously loose electrons. Thus, in this positive charge is increasing while,

Cu half cell continuously receive electrons, thus it goes on collecting negative charge.

Due to collection of positive charge in Zn electrode half cell and collection of negative charge in Cu half cell would stop the reaction.

Salt bridge prevents the net accumulation of charges in either beaker. Thus from negative Cu half cell, negative ions diffuse through the salt bridge into the positive Zn half cell. Thus, it maintains the two solutions electrically neutral.

In voltaic cell, the electric current flow through external circuit. It can be used to light bulb, drive a motor etc.

Reversibility of Galvanic or Voltaic cell

<u>If external circuit is replaced by source of electricity that opposes voltaic cell</u>, then the reaction in voltaic cell will be reversed and <u>electrons flow in opposite direction</u> from Cu to Zn electrode.

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$$
$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-$$
$$Zn^{2+}_{(aq)} + Cu_{(s)} \longrightarrow Zn_{(s)} + Cu^{2+}_{(aq)}$$

Now the cell becomes electrolytic cell, because in this, electricity is being used to carry out <u>non-spontaneous reaction</u>.

Oxidation occurs at Cu electrode and reduction occurs at Zn electrode.

ELECTRODE POTENTIAL

The potential set up when an electrode is in contact with one molar solution of its own ion at 298 K is called Standard Electrode potential or standard reduction potential.

It is denoted by E^o

Examples:

The standard reduction potential of Zn is – 0.76V and that of Cu is +0.34V.

<u>Explanation</u>

When a metal electrode is dipped into the solution of its own ion. There may be two tendencies

Metal atom from electrode leaves the electron on metal and goes into solution. This is oxidation process

$$M \longrightarrow M^+ + e^-$$

Metal ion in solution may take up electrons from the metal electrode and deposit as atom on electrode. Thus it makes electrode +ve

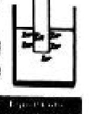
$$M^+ + e^- \longrightarrow M$$

The –ve or +ve nature of electrode relative to solution depends upon the relative tendencies of the two processes.

At last, a dynamic equilibrium is established due to the same rate of two processes. Thus no further potential difference is developed.

<u>Examples</u>

A Zn electrode in a solution containing Zn^{+2} ions becomes negative because Zn has greater tendency to leave electrons metal surface and goes into solution as Zn^{2+} ions.



The negative charge on the Zn rod will attract an atmosphere of positively charged zinc ions around the rod to form an electrical double layer as shown in the fig.

The equilibrium is represented as

$$Zn_{(s)} \rightleftharpoons Zn^{2+}_{(aq)} + 2e^-$$

Standard Oxidation Potential

The potential of an electrode at which oxidation takes place under standard conditions is called standard oxidation potential

e.g. $Zn \longrightarrow Zn^{2+} + 2e^- \quad E^o_{ox} = 0.76$ volts

Standard Reduction Potential

The potential of an electrode at which reduction takes place under standard conditions is called standard reduction potential

It is represented as

$$Cu^{2+} + 2e^- \longrightarrow Cu \qquad E^o_{red} = 0.34 \text{ volts}$$

- For any substance, standard reduction potential is equal to its standard oxidation potential but with opposite signs

  i.e. $E^o_{(red)} = -E^o_{(ox)}$
- The standard electrode potential of hydrogen is taken as zero.

Exercise Q10.

Describe the construction and working of standard hydrogen electrode.

Standard Hydrogen Electrode (SHE)

<u>**Construction**</u>

- A standard hydrogen electrode consists of a <u>platinum foil</u>, <u>electrolytically coated</u> with a layer of <u>finely divided platinum</u> black. It provides <u>large surface area</u>.
- The foil is connected with a <u>platinum wire</u>, enclosed within a <u>glass case</u>. <u>Pure H_2</u> gas passes through this case at <u>1 atm</u>. It is immersed in <u>1M HCl</u> solution.
- The <u>Pt</u> acts as an <u>electrical conductor</u>. It also <u>helps</u> to <u>attain equilibrium</u> between gas and its ions in solution.

$$H_2 \rightleftharpoons 2H^+ + 2e^-$$

- Standard potential of standard hydrogen electrode is arbitrarily taken as zero. Electrode potentials of all other electrodes can be determined by comparing them with SHE.

Working

- SHE can act as both cathode and anode depending upon other electrode with which it is connected.

Following are the reactions of SHE

SHE as Anode: $H_2 \rightarrow 2H^+ + 2e^-$ $E^\circ_{ox} = 0.00$ volts

SHE as Cathode: $2H^+ + 2e^- \rightarrow H_2$ $E^\circ_{red} = 0.00$ volts

Measurement of Electrode Potential

Unfortunately, it is not possible to determine the single electrode potential.

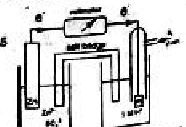
However, the potential of a single electrode can be determined by coupling it with a standard electrode of known potential such as standard hydrogen electrode (SHE) in a galvanic cell. The two solutions are separated by a porous partition or a salt bridge containing conc. solution of KCl. Salt bridge provides a highly conducting path between the two electrolytic solutions. The potential difference is measured by a voltmeter.

Since standard electrode potentials (oxidation and reduction) of SHE are taken as zero. Therefore, the measured value of cell potential will be the potential of unknown electrode.

In this way, a series of standard reduction potential can be built up for different electrodes.

Example 1: Measurement of Zn Electrode Potential

Electrode potential of Zn electrode can be measured by making a galvanic cell. It consists of Zn electrode dipped in 1M solution of its ions and SHE at 25°C. Under the standard conditions, voltmeter shows 0.76 volts and the deflection shows that electrons are flowing from Zn to SHE.



Thus, Zn has greater ability to give up electron than H_2 gas by 0.76 volts.

The reactions are

At Anode (oxidation)

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

At Cathode (reduction)

$$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$$

Since Standard electrode potential of SHE is 0, therefore 0.76 is the standard oxidation potential of Zn.

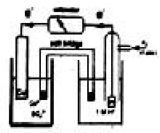
Hence, its standard reduction potential will be −0.76 volts.

Example 2: Measurement of Cu Electrode Potential

Electrode potential of Cu electrode can be measured by making a galvanic cell. It consists of Cu electrode is dipped in 1M solution of its ions and SHE at 25°C. Under the standard conditions, voltmeter shows 0.34 volts and the deflection shows that electrons are flowing from SHE to Cu.

Thus, H_2 has greater ability to give up electron than Cu gas by 0.34 volts.

The reactions are



At Anode (oxidation)

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$$

At Cathode (reduction)

$$Cu_{(s)} + 2e^- \longrightarrow Cu^{2+}_{(aq)}$$

Since Standard electrode potential of SHE is 0, therefore 0.34 is the standard reduction potential of Cu.

Hence, its standard oxidation potential will be −0.34 volts.

THE ELECTROCHEMICAL SERIES

When electrodes are arranged in order of their standard electrode potential on the hydrogen scale, the resulting list is called Electrochemical Series.

According to International Union of Pure and Applied Chemistry (IUPAC), standard electrode potential are given in reduction mode.

The oxidation potential of the electrodes can be obtained by reversing the sign of their reduction potential.

These reduction potential are given under standard conditions. i.e. 25°C and 1 atm pressure and 1 M solution of its ions. Changes in temperature, concentration and pressure will change the values of reduction potential.

A brief sketch of this series is given below

Table (10.2): standard reduction potentials (E°) of element at 298K

Element	Electrode			Standard reduction potential (E°)
Li	$Li^{+} + e^{-}$	$\longrightarrow$	Li	−3.045
K	$K^{+} + e^{-}$	$\longrightarrow$	K	−2.925
Ca	$Ca^{2+} + 2e^{-}$	$\longrightarrow$	Ca	−2.87
Na	$Na^{+} + e^{-}$	$\longrightarrow$	Na	−2.714
Mg	$Mg^{2+} + 2e^{-}$	$\longrightarrow$	Mg	−2.37
Al	$Al^{3+} + 3e^{-}$	$\longrightarrow$	Al	−1.66
Zn	$Zn^{2+} + 2e^{-}$	$\longrightarrow$	Zn	−0.76
Cr	$Cr^{3+} + 3e^{-}$	$\longrightarrow$	Cr	−0.74
Fe	$Fe^{2+} + 2e^{-}$	$\longrightarrow$	Fe	−0.44
Cd	$Cd^{2+} + 2e^{-}$	$\longrightarrow$	Cd	−0.403
Ni	$Ni^{2+} + 2e^{-}$	$\longrightarrow$	Ni	−0.25
Sn	$Sn^{2+} + 2e^{-}$	$\longrightarrow$	Sn	−0.14
Pb	$Pb^{2+} + 2e^{-}$	$\longrightarrow$	Pb	−0.126
H_2	$2H^{+} + 2e^{-}$	$\longrightarrow$	H_2	0.000
Cu	$Cu^{2+} + 2e^{-}$	$\longrightarrow$	Cu	+0.34
Cu	$Cu^{+} + e^{-}$	$\longrightarrow$	Cu	+0.521
I_2	$I_2 + 2e^{-}$	$\longrightarrow$	$2I^{-}$	+0.535
Fe	$Fe^{3+} + 3e^{-}$	$\longrightarrow$	Fe	+0.771
Ag	$Ag^{+} + e^{-}$	$\longrightarrow$	Ag	+0.7994
Hg	$Hg^{2+} + 2e^{-}$	$\longrightarrow$	Hg	+0.885
Br_2	$Br_2 + 2e^{-}$	$\longrightarrow$	$2Br^{-}$	+1.08
Cl_2	$Cl_2 + 2e^{-}$	$\longrightarrow$	$2Cl^{-}$	+1.360
Au	$Au^{3+} + 3e^{-}$	$\longrightarrow$	Au	+1.50
F_2	$F_2 + 2e^{-}$	$\longrightarrow$	$2F^{-}$	+2.87

Increasing strength as an oxidizing agent ↓

Increasing strength as an reducing agent ↑

APPLICATIONS OF ELECTROCHEMICAL SERIES

The emf series has many applications.

1. Prediction of the feasibility of a chemical Reaction

Using standard reduction and oxidation potentials, spontaneity of a cell reaction can be determined.

The cell voltage is determined using the formula

$$E^{0}_{cell} = E^{0}_{(ox)} + E^{0}_{(red)}$$

- If E^{0}_{cell} is <u>positive</u>, cell reaction is <u>spontaneous.</u>
- If E^{0}_{cell} is negative, cell reaction is <u>non-spontaneous.</u>

<u>Example-1</u>

$$Zn \longrightarrow Zn^{2+} + 2e^{-} \qquad E^{0}_{(ox)} = 0.76 \text{ volts}$$

$$\underline{Cu^{2+} + 2e^{-} \longrightarrow Cu \qquad E^{0}_{(red)} = 0.34 \text{ volts}}$$

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu \qquad E^{0}_{cell} = 1.10 \text{ volts}$$

This reaction is spontaneous. However, its reverse reaction will not be spontaneous.

> Thus, Cu^{2+} can oxidize solid Zn, but Zn^{2+} cannot oxidize solid Cu.

2. Calculation of Cell Voltage (emf)

While making Galvanic cell, the <u>electrode above in electrochemical series will act as anode</u>, while <u>the electrode below will act as cathode.</u>

At anode oxidation takes place, at cathode reduction takes place. The cell potential is determined by the formula

$$E^{0}_{cell} = E^{0}_{(ox)} + E^{0}_{(red)}$$

e.g. for Zn – Cu cell

Oxidation potential of Zn is +0.76 volts, while reduction potential of Cu^{2+} is 0.34 volts, thus

$$E^{0}_{cell} = E^{0}_{(ox)} + E^{0}_{(red)} = 0.76 + 0.34 = 1.10 \text{ volts}$$

<u>Electromotive Force (emf)</u>

The cell voltage or emf measures the force with which electrons move in the external circuit.

Thus, it measures the tendency of the cell reaction to takes place. Hence, Galvanic cell gives quantitative measure of the relative tendency of the reactions to occur.

Example: The emf of a Zn-Cu cell is 1.10 volts

3. Comparison of Relative Tendency of Metals and Non-Metals to Get Oxidised or Reduced

Generally

Greater the value of reduction potential of a specie.

Greater is its tendency to accept electron.

Hence it will be a better oxidizing agent

Examples

Ions like Au^{3+}, Pt^{2+}, Hg^{2+}, Ag^{+}, Cu^{2+} and non-metals like F_2, Cl_2, Br_2 and I_2 which lie below SHE have more tendency to accept electrons. Hence, these easily undergo reduction.

emf series show

Strong oxidising agents have large positive values of standard reduction potential. These lie below SHE in the series

While

Strong reducing agents have large negative values of standard reduction potential. These lie above SHE in the series.

4. Relative Chemical Reactivity of Metals

Greater the value of standard reduction potential, lesser is the ability to loose electrons (i.e. to change into positive ions). Hence its reactivity is less, Thus

- Metals like Li, Na, K and Rb are highly reactive.
- Coinage metals Cu, Ag and Au are the least reactive because they have positive reduction potential.
- Metals like Pb, Sn, Ni, Co and Cd which are very close to SHE react very slowly with steam to liberate hydrogen gas.
- Metals like Fe, Cr, Zn, Mn, Al and Mg have more negative reduction potential. Thus, these react with steam to produce metallic oxides and H_2 gas.

5. Reaction of Metals with Dilute Acid

Greater value of reduction potential. Lesser is the ability to loose electron to form positive ion. Hence weaker is its tendency to displace H_2.

Thus any metal above SHE could displace H_2 from acid but those below it can not displace H_2.

Examples

- Metals like Zn, Mg and Cu have negative values of reduction potentials. Thus, these can liberate H_2

  i.e., $Zn + HCl \rightarrow ZnCl_2 + H_2$
- Metals like Au, Pb, Ag and Cu have high positive values of reduction potentials. Thus, these do not liberate H_2

6. Displacement of One Metal by Another from its Solution

Any metal can displace any other metal from its solution, present below in the electrochemical series.

Thus, Fe can displace Cu from $CuSO_4$

$$Fe + CuSO_4 \longrightarrow Cu^{2+} + FeSO_4$$

However, Zn cannot displace Mg from $MgSO_4$

$$Zn + MgSO_4 \longrightarrow \text{No Reaction}$$

MODERN BATTERIES AND FUEL CELLS

These may be of two types

PRIMARY CELLS

These can not be re-charged.

e.g., Alkaline battery, Silver-oxide battery.

SECONDARY CELLS

These can be re-charged

e.g. Lead accumulator.

Difference between Primary and Secondary Cells.

	Primary Cells		Secondary Cells
1	They cannot be recharged	1	They can be recharged
2	They contain electrolyte in an adsorbent or separator. Thus these are called dry cells.	2	They usually contain free-flowing liquid electrolyte in larger amount. Thus these may be called wet cells.
3	They are generally smaller in size	3	They are generally larger in size.
4	They are disposable	4	They require regular maintenance and recharging
5	Examples: Alkaline battery, Silver-oxide battery.	5	Examples: Lead Accumulator

LEAD ACCUMULATOR (RECHARGEABLE)

It is a re-chargeable car battery

Construction

A fully charged battery consists of

<u>A cathode of lead oxide (PbO_2)</u>

<u>And Anode of Metallic Lead</u>

<u>The electrolyte is 30% H_2SO_4 with density 1.25 g/cm^3.</u>

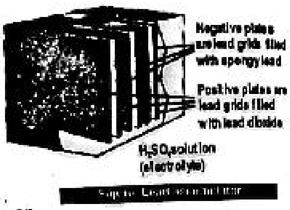


Fig: Lead accumulator

Two electrodes are connected through an external circuit. It produces electrical current by <u>discharging</u>.

Working and Reaction

It produces electric current by discharging

Discharging

<u>At Anode (oxidation)</u>

At anode, lead atoms loose electrons and oxidise to Pb^{2+}. Pb^{2+} ions combine with SO_4^{2-} ions and deposit as $PbSO_4$ on anode.

$$Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$$

The electrons released pass through an external circuit and thus produce electricity.

<u>At Cathode (reduction)</u>

PbO_2 receive electrons from anode. It then gives redox reaction with H^+ ions in the electrolyte to give lead ions and water.

$$PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O_{(l)}$$

The Pb^{2+} ions then combine with the SO_4^{2-} and deposit as $PbSO_4$ on cathode.

<u>The overall reaction is</u>

$$Pb_{(s)} + PbO_{2(s)} + 4H^+{}_{(aq)} + 2SO_4^{2-}{}_{(aq)} \longrightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

Thus, electron flows through external circuit and can be used to light bulb etc. <u>A single cell produce about 2 volts.</u>

<u>When both electrodes are completely covered by $PbSO_4$, reaction stops and no more current is produced. The battery is then recharged</u>

Re-charging

During this, anode of the external electrical source is connected to anode of cell while cathode is connected with cathode of the cell.

Thus, redox reactions are reversed.

<u>*At Anode (This becomes cathode and reduction occurs during re-charging)*</u>

$$PbSO_{4(s)} + 2e^- \longrightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$$

<u>*At Cathode (This becomes anode and oxidation occurs during re-charging)*</u>

$$PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^-$$

<u>*Overall Reaction*</u>

$$2PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow Pb_{(s)} + PbO_{2(s)} + 4H^+{}_{(aq)} + 2SO_4^{2-}{}_{(aq)}$$

During discharging, the conc. of acid falls and its density decreases to 1.15 g/cm^3. During re-charging concentration of acid goes back to 1.25 g/cm^3 and voltage of cell is come back to around 2 volts.

Uses

It is mainly used as car battery for starting engine, for lightening up car lights etc.

TYPICAL CAR BATTERY

- A typical car battery consists of <u>six cells</u>, connected in <u>series</u>.
- Each cell gives <u>2V</u>.
- Each cell contains two <u>lead grids</u> packed with the electrode materials.
- The <u>anode</u> is spongy lead and cathode is <u>powdered PbO_2</u>.
- The grid is immersed in an electrolytic solution of nearly <u>4.5 M</u> H_2SO_4 (30%). <u>Fibre glass</u> sheets between the grids prevent shorting by accidental physical contact.

When the cell is discharged, it generates electric energy as voltaic cell.

ALKALINE BATTERY (NON-RECHARGEABLE)

Construction

It is a dry alkaline cell.

It uses Zn and MnO_2 as reactants.

<u>Zn rod acts as anode.</u>, while

<u>MnO_2 acts as cathode</u>

<u>Electrolyte consists of KOH solution.</u>

<u>Therefore, it is alkaline.</u>

The battery is enclosed in a steel container.

Zn electrode is slightly porous to give larger effective area. It allows cell to deliver more current than common dry cell. It also has longer life.

Working and Reactions

Its reactions are

At Anode (oxidation)

$$Zn_{(s)} + 2\,OH^-_{(aq)} \longrightarrow Zn(OH)_{2(s)} + 2e^-$$

At cathode (reduction)

$$2MnO_{2(s)} + H_2O_{(l)} + 2e^- \longrightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}$$

The overall reaction is

$$Zn(s) + 2MnO_{2(s)} + H_2O_{(l)} \longrightarrow Mn_2O_{3(s)} + Zn(OH)_{2(s)}$$

Cell voltage is 1.5 V

SILVER OXIDE BATTERY

It is used as power source in electronic devices e.g. watches, auto exposure cameras and electronic calculators. It is very small in size.

Construction

The cathode is of silver oxide Ag_2O.

The anode is of Zn metal.

The electrolyte is basic.

Working and Reactions

Following reactions occur

At anode (oxidation)

$$Zn_{(s)} + 2OH^-_{(aq)} \longrightarrow Zn(OH)_{2(s)} + 2e^-$$

At cathode (reduction)

$$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \longrightarrow 2Ag_{(s)} + 2OH^-_{(aq)}$$

The overall reaction is

$$Ag_2O_{(s)} + H_2O_{(l)} + Zn(s) \longrightarrow 2Ag_{(s)} + Zn(OH)_{2(s)}$$

Voltage of battery is 1.5 V

NICKEL CADMIUM CELL (RECHARGEABLE)

It is a strong cell largely used in NICAD or Nickle Cadmium battery.

Construction

The anode is of Cadmium.

The cathode is of NiO_2.

The electrolyte is alkaline.

Working and Reactions

Following reactions occur

At Anode (oxidation)

$$Cd_{(s)} + 2OH^-_{(aq)} \longrightarrow Cd(OH)_{2(s)} + 2e^-$$

At cathode (reduction)

$$NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \longrightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)}$$

Net Reaction

$$Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \longrightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)}$$

Voltage of the cell is about 1.4 V

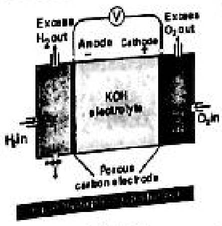
In this, solid reaction products are deposited on electrodes like lead battery. Thus, reaction is easily reversed during recharging. Since no gases are produced during charging or recharging, therefore, it can be sealed. It is light weight.

Uses

- It is used in battery operated tools and portable computers.
- It is also used in cordless razors, photoflash units.

FUEL CELLS

In these cells, fuel gases H_2 and O_2 are reacted and electricity is obtained.



Construction

Electrodes consists of hollow tubes made of porous compressed carbon coated with Pt.

Pt acts as catalyst.

Electrolyte is KOH.

Working

In a common fuel cell, H_2 is oxidized to H_2O and O_2 is reduced to OH^- ions.

<u>At Anode (oxidation)</u>

$$H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(l)} + 2e^-] \times 2$$

<u>At Cathode (reduction)</u>

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$$

<u>Overall reaction</u>

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$$

- These cells run continuously as long as reactants are supplied.
- These cells are operated at high temperature.
- These are used in space vehicles. Water is formed as by product. It may be condensed and used for drinking. Thus Fuel cells produce electricity and pure water during space flights.
- To get several Kilowatts of power, many fuel cells are connected together.
- Fuel cells are very efficient. They convert about 75% of fuels bond energy into electricity.
- Fuel cells are light, portable and sources of electricity.
- Many fuel cells do not produce pollutants.
- Some other cell reactions in fuel cells are
  1. $2NH_3 + 3/2\,O_2 \longrightarrow N_2 + 3H_2O$
  2. $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$
  3. $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

OBJECTIVE AND SHORT ANSWER, QUESTIONS (Exercise)

Q1. *Multiple choice questions.*

(i) The cathodic reaction in the electrolysis of dil. H_2SO_4 with Pt electrode is

(a) reduction (b) oxidation
(c) both oxidation and reduction (d) Neither oxidation nor reduction

(D.G. Khan Board, 2009) (Faisalabad Board, 2009) (Sargodha Board, 2011) (D.G. Khan Board, 2012) (Gujranwala Board, 2012)

(ii) Which of the following statement is correct about galvanic cell.

(a) anode is negatively charged (b) reduction occurs at anode
(c) cathode is positively charged (d) reduction occurs at cathode

(D.G. Khan Board, 2012) (Sargodha Board, 2012) (Lahore Board, 2013)

(iii) Stronger the oxidizing agent, greater is the

(a) oxidation potential (b) reduction potential
(c) redox potential (d) EMF of cell

(Rawalpindi Board, 2010; Gujranwala Board, 2013, 2014) (Sargodha Board, 2014)

(iv) If the salt bridge is not used between two half cells, then the voltage

(a) decrease rapidly (b) decrease slowly
(c) does not change (d) drops to zero

(Faisalabad Board, 2007) (Bahawalpur Board, 2009) (D.G. Khan Board, 2009) (D.G. Khan Board, 2012) (Rawalpindi Board, 2012) (Multan Board, 2011, 2012) (Sargodha Board, 2012)

(v) If a strip of Cu metal is placed in a solution of $FeSO_4$

(a) Cu will be precipitated out (b) Fe is precipitated out
(c) Cu and Fe both dissolve (d) No reaction takes place

(Sargodha Board, 2009, 2013) (Rawalpindi Board, 2012) (Gujranwala Board, 2013)

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (a)
Reduction always occurs at cathode. In dilute H_2SO_4 solution, H^+ ions are present. These ions are reduced at cathode to produce hydrogen gas.
i.e. $2H^+ + 2e^- \longrightarrow H_2$

(ii) Ans: (d)
Reduction always occurs at cathode, while oxidation always occurs at anode.

(iii) Ans: (b)
Substances, which oxidize other substances, are themselves reduced. Therefore, substances, which have greater value of reduction potential, are stronger oxidizing agent.

(iv) Ans: (d)
In the absence of a salt bridge, two half cells cannot make electrical contact. Therefore, the electrolytic conduction is stopped and metallic conduction is also stopped. Thus, voltage drops to zero.

(v) Ans: (d)
Cu is below in electrochemical series than Fe^{2+}. Therefore, it cannot displace Fe^{2+} from $FeSO_4$. Hence no reaction occurs.

Q2. Fill in the blanks with suitable words.

(i) The oxidation number of O atom is ____ in OF_2 and is ______ in H_2O_2.

(ii) Conductivity of metallic conductors is due to the flow of ______, while that of electrolytes is due to flow of ______.

(iii) Reaction taking place at the ______ is termed as oxidation, and at the ______ is called reduction.

(iv) ______ is setup when a metal is dipped in its own ions.

(v) Cu metal ______ the Cu-cathode when electrolysis is performed for $CuSO_4$ solution with Cu-cathodes.

(vi) The reduction potential of Zn is ______ volts and its oxidation potential is ______ volts.

(vii) In a fuel cell ______ react together in the presence of ______

Answers:
(i) +2, -1 (ii) electrons, ions (iii) anode, cathode
(iv) equilibrium (v) deposits on (vi) – 0.76, +0.76
(vii) H_2 and O_2, Pt catalyst

Q3. Indicate TRUE or FALSE as the case may be.

(i) In electrolytic conduction electrons flow through the electrolyte.

(ii) In the process of electrolysis, the electrons in the external circuit flow from cathode to anode.

(iii) Sugar is a non-electrolyte in solid form and when dissolved in water will allow the passage of an electric current.

(iv) A metal will only allow the passage of an electric current when it is in cold state.

(v) The electrolytic products of aqueous copper (II) chloride solution are copper and chlorine.

(vi) Zinc can displace iron form its solution.

(vii) SHE acts as cathode when connected with Cu electrode.

(viii) A voltaic cell produces electrical energy at the expense of chemical energy.

(ix) Lead storage battery is not reversible cell.

(x) Cr changes its oxidation number when $K_2Cr_2O_7$ is reacted with HCl.

Answers:
(i) False (ii) False (iii) False (iv) False (v) True
(vi) True (vii) False (viii) True (ix) False (x) True

Q7. Describe the electrolysis of molten sodium chloride, and a concentrated solution of sodium chloride.

Solved on Page 575

Q8. What is the difference between single electrode potential and standard electrode potential? How can it be measured? Give its importance.

	SINGLE ELECTRODE POTENTIAL		STANDARD ELECTRODE POTENTIAL
1	The potential set up when an electrode is in contact with solution of its own ion is called Single Electrode Potential.	1	The potential set up when an electrode is in contact with one molar solution of its own ion at 298 K is called Standard Electrode potential.
2	It is measured at any condition of temperature, pressure and concentration.	2	It is measured under standard conditions i.e., 25°C, 1 molar solution and 1 atm pressure of gas used.
3	It is denoted by E.	3	It is denoted by E°.
4	The electrochemical series is not based upon single electrode potential	4	The electrochemical series is based upon standard electrode potential

Q9. Outline the important applications of electrolysis. Also write the electrochemical reactions involved therein. Discuss the electrolysis of $CuSO_4$ using Cu electrode and $AgNO_3$ solutions using Ag electrode.

Q10. Describe the construction and working of standard hydrogen electrode.

Solved on Page 579

Q11. Is the reaction $Fe^{3+} + Ag \rightarrow Fe^{2+} + Ag^{+}$ spontaneous? If not, write spontaneous reaction involving these species.

Solution

$$Fe^{3+} + Ag^{+} \longrightarrow Fe^{2+} + Ag^{+}$$

In this reaction, Fe is reduced while Ag is oxidized. Therefore, Fe^{3+} will act as cathode while Ag^{+} as anode.

Thus, emf of the cell will be

$$E^{\circ}_{cell} = E^{\circ}_{ox} + E^{\circ}_{red}$$
$$E^{\circ}_{cell} = -0.7994 + (-0.44)$$
$$E^{\circ}_{cell} = -0.7994 - 0.44$$

$$E^{\circ}_{cell} = \boxed{-1.2394}$$

Since emf of cell is negative, therefore, the cell-reaction is non-spontaneous.

But if the electrodes are reversed, the cell- reaction becomes spontaneous i.e.,

$$Fe^{2+} + Ag^{+} \longrightarrow Fe^{3+} + Ag^{+}$$

For this

$$E^{\circ}_{cell} = \boxed{+1.2394}$$

Q12. Explain the difference between

(a) Ionization and electrolysis

Sr.	IONIZATION	Sr.	ELECTROLYSIS
1	The process in which ionic compounds when fused or dissolved in water split up into charged particles called ions.	1	The process in which electricity is used to carry out a non-spontaneous reaction is called electrolysis.
2	Electrodes are not needed	2	Electrodes are required
3	Electricity is not needed	3	Electricity is required
4	Since there are no electrodes, therefore, ions do not move towards electrodes	4	Ions moves towards their respective electrodes
5	After ionization, ions are not discharged	5	Ions are discharged at electrodes to give neutral products.

(b) Electrolytic and Voltaic (or Galvanic) cell

(Faisalabad Board, 2007; Multan Board, 2009, 2010, 2011; Gujranwala Board, 2010; Lahore Board, 2011, 2014; Azad Kashmir Board, 2012; Sargodha Board, 2012)

Sr.	ELECTROLYTIC CELL	Sr.	VOLTAIC CELL
1	The electrochemical cell in which electrical energy is converted into chemical energy	1	The electrochemical cell in which chemical energy is converted into electrical energy
2	In this cell, a non-spontaneous reaction is carried out with the help of electricity	2	In this spontaneous reaction is used to produce electricity
3	In this cell, chemicals are the products	3	In this cell, electricity is the product
4	Example: Down's Cell, Nelson's Cell	4	Examples: Alkaline battery, Nickle-Cadmium battery.

(c) Conduction through metals (Metallic Conduction) and molten electrolytes (Electrolytic Conduction)

(Lahore Board, 2014)

Sr.	CONDUCTION THROUGH METALS	Sr.	CONDUCTION THROUGH MOLTEN ELECTROLYTE
1	Electrical conduction takes place due to free electrons.	1	Electrical conduction takes palce due to ions.
2	There is no need to convert metal into molten state.	2	Electrolyte must be converted into molten state for electrical conduction.
3	In this case, conductance decreases with increase in temperature.	3	In this case, conductance increases with increase in temperature.
4	No chemical reaction occurs during conduction.	4	Chemical reactions occurs take place during conduction.
5	Chemical composition of metal is not changed during conduction and no new substances are produced.	5	Since chemical reactions occur, therefore, new substances are produced.
6	Example: All metals are conductors. e.g. Fe, Pb etc.	6	Example: Molten Salts e.g. NaCl(l) or their aqueous solutions, acids, bases etc.

Q13. Describe a galvanic cell explaining the function of electrodes and salt bridge.

Solved on Page 576

Q14. Write comprehensive notes on

(a) **Spontaneity of oxidation-reduction reactions.**

Solved on Page 583

(b) **Electrolytic conduction**

Solved on Page 570

(c) **Alkaline, Silver oxide and Nickle-Cadmium batteries, fuel cells.**

Solved on Page 587, 588, 589, 589

(d) **Lead accumulator, its desirable and undesirable features.**

Solved on Page 586

Q15. Will the reaction be spontaneous for the following set of half reactions. What will be the value of Ecell?

(i) $Cr^{3+}_{(aq)} + 3e^- \longrightarrow Cr_{(s)}$

(ii) $MnO_{2(s)} + 4H^+ + 2e^- \longrightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)}$

Standard reduction potential for reaction (i) = −0.74V and for the reaction (ii) = +1.28V.

In reaction (i) Cr is reduced from +3 to 0.

In reaction (ii) Mn is also reduced from +4 to +2.

Both are reduction reactions, hence these reactions are not possible in these forms.

However, if reaction (i) is reversed so that Cr is oxidized then the reaction becomes spontaneous and its emf can be calculated as

(i) $Cr_{(s)} \longrightarrow Cr^{3+}_{(aq)} + 3e^-$ $E^0_{ox} = +0.74\ V$

(ii) $MnO_{2(s)} + 4H^+ + 2e^- \longrightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)}$ $E^0_{red} = +1.28\ V$

emf of the cell is given by

$$E^\circ_{cell} = E^\circ_{oxi} + E^\circ_{red}$$
$$E^\circ_{cell} = +0.74 + 1.28$$
$$E^\circ_{cell} = \boxed{2.02\ V}$$

Q16. Explain the following with reasons

(a) A porous plate or a salt bridge is not required in lead storage cell.

(Lahore Board, 2009, 2010: Sargodha Board, 2007, 2009, 2014: Faisalabad Board, 2007, 2011: Bahawalpur Board, 2011: D.G. Khan Board, 2012: Rawalpindi Board, 2012: Multan Board, 2012)

A salt bridge has two main functions

- It joins the solutions of two half cells and thus complete the circuit.
- It maintains electrical neutrality of the two half cells as ions can pass through it.

In Lead storage battery, both cathode and anode are dipped in the same solution. Therefore, excess positive or negative ions are not produced in the solution. Hence, there is no need of salt bridge.

(b) The standard oxidation potential of Zn is 0.76 V and its reduction potential is -0.76 V. *(Lahore Board, 2008: D.G. Khan Board, 2010)*

According to the law of conservation of energy, energy can neither be created nor destroyed. Therefore, if standard oxidation potential of Zn is 0.76 V, then its potential for reverse process, i.e. standard reduction potential will also be same but with positive sign. Thus

$Zn \rightarrow Zn^{2+} + 2e^-$ $E^0_{ox} = 0.76\ V$

$Zn^{2+} + 2e^- \rightarrow Zn$ $E^0_{red} = -0.76\ V$

(c) Na and K can displace hydrogen from acids but Pt, Pd and Cu cannot.

(Rawalpindi Board, 2007: Gujranwala Board, 2009: Bahawalpur Board, 2009: Faisalabad Board, 2011: D.G. Khan Board, 2011: Azad Kashmir Board, 2012: Sargodha Board, 2012, 2014)

Zn can displace hydrogen from acids but Cu cannot do so. Why? ***(Gujranwala Board, ... (Rawalpindi Board, 2013)***

Na can displace hydrogen from acids but Cu cannot. Why? ***(Multan Board, 2011)***

Greater the value of reduction potential, Lesser is the ability to loose electron to form positive ion, Hence weaker is its tendency to displace H_2.

- Metals like Pt, Pb, and Cu have high positive value of reduction potential. Thus these do not liberate H_2
- Metals like Na and K have negative values of reduction potential. Thus, these can liberate H_2.

$2Na + 2HCl \rightarrow 2NaCl + H_2$

$2K + 2HCl \rightarrow 2KCl + H_2$

(d) The equilibrium is set up between metal atoms of electrode and ions of metal in a cell.

When a metal electrode is dipped in the solution of its own ions. There may be two tendencies

Metal atom from electrode leaves the electron on metal and goes into solution. This is oxidation process

$$M \longrightarrow M^+ + e^-$$

Metal ions in solution may take up electrons from the metal electrode and deposit as atoms on electrode. This is reduction process.

$$M^+ + e^- \longrightarrow M$$

At last, a dynamic equilibrium is established due to same rate of two processes. The potential set up when an electrode is in contact with solution of its own ion is called Electrode Potential.

(e) A salt bridge maintains the electrical neutrality in the cell.

(Rawalpindi Board, 2011: Lahore Board, ... Faisalabad Board, 2010: D.G. Khan Board, 2010: Gujranwala Board, 2010: Board, 2012: Azad Kashmir Board, 2012: Multan Board, 2009, 2012)

Two half cells are electrically connected by a salt bridge.

Consider a Zn-Cu cell

During reactions of this cell, Zn half cell continuously loose electrons. Thus, in this positive charge is increasing.

$$Zn \rightarrow Zn^{2+} + 2e^-$$

While, Cu half cell continuously receive electrons, thus it goes on collecting negative charge.

$$Cu^{2+} + 2e^- \rightarrow Cu$$

Collection of positive charge in Zn electrode half cell and collection of negative charge in Cu half cell would stop the reaction.

Salt bridge prevents the net accumulation of charges in either beaker. Thus from negative Cu half cell, negative ions diffuse through the salt bridge into the positive Zn half cell. In this way, salt bridge maintains the two solutions, electrically neutral.

(f) Lead accumulator is a chargeable battery.

(Rawalpindi Board, 2010: Multan Board, 2012: Lahore Board, 2013: Sargodha Board, 2013)

OR *Explain through equations how lead battery is recharged? (Lahore Board, 2011)*

For recharging of Lead Accumulator, the anode of the external electrical source is connected to anode of cell while cathode is connected with cathode of the cell.

Thus, redox reactions are reversed.

<u>At Anode (This becomes cathode and reduction occurs during re-charging)</u>

$$PbSO_{4(s)} + 2e^- \longrightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$$

<u>At Cathode (This becomes anode and oxidation occurs during re-charging)</u>

$$PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow PbO_{2(s)} + 4H^+_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^-$$

<u>Overall Reaction</u>

$$2PbSO_{4(s)} + 2H_2O_{(l)} \longrightarrow Pb_{(s)} + PbO_{2(s)} + 4H^+_{(aq)} + 2SO_4^{2-}{}_{(aq)}$$

During discharging, the conc. of acid falls and its density decreases to 1.15 g/cm³. During re-charging concentration of acid goes back to 1.25 g/cm³ and voltage of cell is come back to around 2 volts.

(g) Impure Cu can be purified by electrolytic process.

(Gujranwala Board, 2009: D.G. Khan Board, 2009: Lahore Board, 2012: Bahawalpur Board, 2012: Faisalabad Board, 2013: Gujranwala Board, 2014)

Impure Cu can be made pure in an electrolytic cell. Thick sheets of impure copper are made anode, while, thin sheets of pure copper are made cathode in the cell. These sheets are placed in an electrolytic solution of $CuSO_4$.

When current is passed through the cell, Cu from anode is oxidized to Cu^{2+} ions, which go into the solution. From the solution, Cu^{2+} ions are reduced to metallic Cu and deposits as pure Cu on cathode. In this way, impure sheets of Cu (anode) become thin, while pure sheets of pure Cu (cathode) become thick.

The reactions in the cell are

<u>At Anode (oxidation)</u>

$$Cu \longrightarrow Cu^{2+} + 2e^-$$

<u>At Cathode (reduction)</u>

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Thus, there is no net reaction in the cell. However, the net result is the purification of Cu.

(h) S.H.E. acts as anode when connected with the Cu electrode but as cathode with Zn electrode.

(Multan Board, 2006, 2011: Sargodha Board, 2010)

1. S.H.E. (0.0 volts) has higher reduction potential then Zn (– 0.76 volts). Thus, when both these are connected electron flows from Zn to S.H.E. Hence, Zn acts as anode and S.H.E. as cathode.
2. S.H.E. (0.0 volts) has lower reduction potential then Cu (+ 0.34 volts). Thus, when both these are connected electron flows from S.H.E. to Cu. Hence, S.H.E. acts as anode and Cu as cathode.

NUMERICAL PROBLEMS *(Exercise)*

Q 4 (c) Calculate the oxidation number of Chromium in the following.

$CrCl_3$ *(Lahore Board, 2010: Multan Board, 2012)*

Oxidation number of Cl = –1
Oxidation number of Cr = x
Oxidation number of Cr can be calculated as
For $CrCl_3$
$x + 3(-1) = 0$
$x - 3 = 0$
or $x = +3$

K_2CrO_4

Oxidation number of K = +1
Oxidation number of O = –2
Oxidation number of Cr = x
Thus
For K_2CrO_4
$2(+1) + x + 4(-2) = 0$
$x - 6 = 0$
or $x = +6$

$K_2Cr_2O_7$

Oxidation number of K = +1
Oxidation number of O = –2
Oxidation number of Cr= x
Thus
For $K_2Cr_2O_7$
$2(+1) + 2x + 7(-2) = 0$
$2x - 12 = 0$
or $x = +12/2 = +6$

(Lahore Board, 2006: D.G. Khan Board, 2008: Gujranwala Board, 2013: Bahawalpur Board, 2011)

CrO_3

Oxidation number of O = –2
Oxidation number of Cr = x
Thus
For CrO_3
$x + 3(-2) = 0$
$x - 6 = 0$
or $x = +6$

(Gujranwala Board, 2009: Faisalabad Board, 2010)

(Faisalabad Board, 2007: Bahawalpur Board, 2012: Lahore Board, 2013)

Cr_2O_3

Oxidation number of O = –2
Oxidation number of Cr= x
Thus
For Cr_2O_3
$2x + 3(-2) = 0$
$2x - 6 = 0$
or $x = +6/2 = +3$

$Cr_2O_7^{2-}$

Oxidation number of O = –2
Oxidation number of Cr= x
Thus
For $Cr_2O_7^{2-}$
$2x + 7(-2) = -2$
$2x - 14 = -2 + 14$
or $x = +12/2 = +6$

(Lahore Board, 2010: Multan Board, 2012) (Faisalabad Board, 2007: Bahawalpur Board, 2012: Lahore Board, 2013)

$Cr_2(SO_4)_3$

Oxidation number of S = +6
Oxidation number of O = –2
Oxidation number of Cr= x
Thus
For $Cr_2(SO_4)_3$
$2x + 3[(+6) + 4(-2)] = 0$
$2x - 6 = 0$
or $x = 6/2 = +3$

(Bahawalpur Board, 2011)

(d) Calculate the oxidation numbers of the elements underlined in the following compounds

$Na_3\underline{P}O_4$ *(Rawalpindi Board, 2010, 2013)*

Oxidation number of Na = +1
Oxidation number of O = −2
Oxidation number of P = x

For Na_3PO_4

$3(+1) + x + 4(-2) = 0$
$x - 5 = 0$
or $x = +5$

$Na_2\underline{C}O_3$

Oxidation number of O = −2
Oxidation number of Na = +1
Oxidation number of C = x
Thus

For Na_2CO_3

$2(+1) + x + 3(-2) = 0$
$x - 4 = 0$
or $x = +4$

$Cr_2(\underline{S}O_4)_3$

Oxidation number of Cr = +3
Oxidation number of O = −2
Oxidation number of S = x
Thus

For $Cr_2(SO_4)_3$

$2(+3) + 3[(x) + 4(-2)] = 0$
$3x - 18 = 0$
or $x = 18/3 = +6$

$Ca(\underline{Cl}O_3)_2$ *(Multan Board, 2006)*

Oxidation number of Ca = +2
Oxidation number of O = −2
Oxidation number of Cl = x
Thus

For $Ca(ClO_3)_2$

$(+2) + 2[x + 3(-2)] = 0$
$2 + 2x - 12 = 0$
or $x = 10/2 = +5$

$K_2\underline{Mn}O_4$

Oxidation number of K = +1
Oxidation number of O = −2
Oxidation number of Mn = x
Thus

For K_2MnO_4

$2(+1) + x + 4(-2) = 0$
$x - 6 = 0$
or $x = +6$

$H\underline{N}O_3$ *(Faisalabad Board, 2011)*

Oxidation number of H = +1
Oxidation number of O = −2
Oxidation number of N = x
Thus

For HNO_3

$(+1) + x + 3(-2) = 0$
$x - 5 = 0$
or $x = +5$

$H\underline{P}O_3$ *(Rawalpindi Board, 2010)*

Oxidation number of H = +1
Oxidation number of O = −2
Oxidation number of P = x
Thus

For HPO_3

$(+1) + x + 3(-2) = 0$
$x - 5 = 0$
or $x = +5$

Try Yourself

$H_2\underline{O}_2$, $Ca(O\underline{Cl})_2$, $Na\underline{I}O_3$, $\underline{Zn}(OH)_2$, $H_3\underline{P}O_4$, $Na\underline{Cl}$

Q5 (b) Balance the following equations by oxidation number method.

$$HNO_3 + HI \longrightarrow NO + I_2 + H_2O$$ *(Gujranwala Board, 2013)*

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$\overset{+1}{H}\overset{+5}{N}\overset{3(-2)}{O_3} + \overset{+1}{H}\overset{-1}{I} \longrightarrow \overset{+2}{N}\overset{-2}{O} + \overset{0}{I_2} + H_2O$$

- Determine the no. of electrons gained and lost and equate them.

gain of $3e^- \times 1 = 3e^-$ (reduction)

$$H\overset{+5}{N}O_3 + H\overset{-1}{I} \longrightarrow \overset{+2}{N}O + \overset{0}{I_2} + H_2O$$

loss of $1e^- \times 3 = 3e^-$ (oxidation)

- Balance loss and gain of electrons by multiplying HI by 3.

$$HNO_3 + 3HI \longrightarrow NO + I_2 + H_2O$$

- Balance the rest of equation by inspection method.

$$2HNO_3 + 6HI \longrightarrow 2NO + 3I_2 + 4H_2O$$

$$Br_2 + NaOH \longrightarrow NaBrO_3 + NaBr + H_2O$$ *(Sargodha Board, 2013)*

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$\overset{0}{Br_2} + \overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} \longrightarrow \overset{+1}{Na}\overset{+5}{Br}\overset{3(-2)}{O_3} + \overset{+1}{Na}\overset{-1}{Br} + H_2O$$

- Since Br_2 is involved both in oxidation and reduction, therefore, we shall write the Br_2 twice. Then determine the no. of electrons gained and lost and equate them.

gain of $2(1)e^- \times 5 = 10e^-$ (reduction)

$$\overset{0}{Br_2} + \overset{0}{Br_2} + NaOH \longrightarrow \overset{+1}{Na}\overset{+5}{Br}\overset{3(-2)}{O_3} + \overset{+1}{Na}\overset{-1}{Br} + H_2O$$

loss of $2(5)e^- \times 1 = 10e^-$ (oxidation)

- Balance loss and gain of electrons by multiplying Br_2 by 5, in which oxidation occurs.

$$5Br_2 + Br_2 + NaOH \longrightarrow NaBrO_3 + NaBr + H_2O.$$

- Balance the rest of equation by inspection method.

$$5Br_2 + Br_2 + 12NaOH \longrightarrow 2NaBrO_3 + 10NaBr + 6H_2O$$

Or $6Br_2 + 12NaOH \longrightarrow 2NaBrO_3 + 10NaBr + 6H_2O$

Or $3Br_2 + 6NaOH \longrightarrow NaBrO_3 + 5NaBr + 3H_2O$

$Zn + HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$ **(NOTE: Cu may be present in place of Zn)**

(Gujranwala Board, 2011; Multan Board, 2012; Sargodha Board, 2011)

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$\overset{0}{Zn} + \overset{+1\,+5\,3(-2)}{HNO_3} \longrightarrow \overset{+2\,+5}{Zn(NO_3)_2} + \overset{+2\,-2}{NO} + H_2O$$

- In this eq. N is reduced from +5 in HNO_3 to +2 in NO. But it's oxidation state is not changed in $Cu(NO_3)_2$. Therefore, write HNO_3 twice and determine the number of electrons gained and lost and equate them.

gain of $3e^- \times 2 = 6e^-$ (reduction)

$$HNO_3 + \overset{0}{Zn} + \overset{+5}{HNO_3} \longrightarrow \overset{+2\,+5}{Zn(NO_3)_2} + \overset{+2\,-2}{NO} + H_2O$$

loss of $2e^- \times 3 = 6e^-$ (oxidation)

- Use the multiplier obtained above to balance loss and gain of electrons. Thus Cu is multiplied by 3 and HNO_3 by 2.

$$HNO_3 + 3Zn + 2HNO_3 \longrightarrow Zn(NO_3)_2 + NO + H_2O$$

- Balance the rest of equation by inspection method.

$$6HNO_3 + 3Zn + 2HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

or

$$3Zn + 8HNO_3 \longrightarrow 3Zn(NO_3)_2 + 2NO + 4H_2O$$

$MnO_2 + HCl \longrightarrow MnCl_2 + H_2O + Cl_2$ ***(Sargodha Board, 2012)***

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$\overset{+4\,2(-2)}{MnO_2} + \overset{+1\,-1}{HCl} \longrightarrow \overset{+2\,2(-1)}{MnCl_2} + H_2O + \overset{0}{Cl_2}$$

- In this eq. Cl is reduced from −1 in HCl to 0 in Cl_2. But it's oxidation state is not changed in $MnCl_2$. Therefore, write HCl twice and determine the no. of electrons gained and lost and equate them.

gain of $2e^- \times 1 = 2e^-$ (reduction)

$$HCl + \overset{+4}{MnO_2} + \overset{-1}{HCl} \longrightarrow \overset{+2\,2(-1)}{MnCl_2} + H_2O + \overset{0}{Cl_2}$$

loss of $1e^- \times 2 = 2e^-$ (oxidation)

- Use the multiplier obtained above to balance loss and gain of electrons.

$$HCl + MnO_2 + 2HCl \longrightarrow MnCl_2 + H_2O + Cl_2$$

- Balance the rest of equation by inspection method.

$$2HCl + MnO_2 + 2HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

or

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$$

$FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$\overset{+2}{FeSO_4} + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3 + \overset{+3}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O$$

- Determine the no. of electrons gained and lost and equate them.

gain of $2(3)e^- \times 1 = 6e^-$ (reduction)

$$\overset{+2}{FeSO_4} + K_2\overset{+6}{Cr_2}O_7 + H_2SO_4 \longrightarrow \overset{+3}{Fe_2}(SO_4)_3 + \overset{+3}{Cr_2}(SO_4)_3 + K_2SO_4 + H_2O$$

loss of $1e^- \times 6 = 6e^-$ (oxidation)

- Use the multiplier obtained above to balance loss and gain of electrons

$$6FeSO_4 + K_2Cr_2O_7 + H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

- Balance the rest of equation by inspection method.

$$6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + 7H_2O$$

$Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$\overset{0}{Cu} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{+2}{Cu}SO_4 + \overset{+4\,2(-2)}{SO_2} + H_2O$$

- In this equation S is reduced from +6 in H_2SO_4 to +4 in SO_2. But it's oxidation state is not changed in $CuSO_4$. Therefore, write H_2SO_4 twice and determine the no. of electrons gained and lost and equate them.

gain of $2e^- \times 1 = 2e^-$ (reduction)

$$H_2SO_4 + \overset{0}{Cu} + H_2\overset{+6}{S}O_4 \longrightarrow \overset{+2}{Cu}SO_4 + \overset{+4}{S}O_2 + H_2O$$

loss of $2e^- \times 1 = 2e^-$ (oxidation)

- Use the multiplier obtained above to balance loss and gain of electrons.

$$H_2SO_4 + Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + H_2O$$

- Balance the rest of equation by inspection method.

$$H_2SO_4 + Cu + H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

Or

$$Cu + 2H_2SO_4 \longrightarrow CuSO_4 + SO_2 + 2H_2O$$

$$H_2SO_4 + HI \longrightarrow SO_2 + I_2 + H_2O$$

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$H_2\overset{+6}{S}O_4 + \overset{+1-1}{HI} \longrightarrow \overset{+4}{S}O_2 + \overset{0}{I_2} + H_2O$$

- Determine the no. of electrons gained and lost and equate them.

gain of $2e^- \times 1 = 2e^-$ (reduction)

$$H_2\overset{+6}{S}O_4 + H\overset{-1}{I} \longrightarrow \overset{+4}{S}O_2 + \overset{0}{I_2} + H_2O$$

loss of $1e^- \times 2 = 2e^-$ (oxidation)

- Use the multiplier obtained above to balance loss and gain of electrons

$$H_2SO_4 + 2HI \longrightarrow SO_2 + I_2 + H_2O$$

- Balance the rest of equation by inspection method.

$$H_2SO_4 + 2HI \longrightarrow SO_2 + I_2 + 2H_2O$$

$$NaCl + MnO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$$

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$\overset{+1\ -1}{NaCl} + \overset{+4\ 2(-2)}{MnO_2} + H_2SO_4 \longrightarrow Na_2SO_4 + \overset{+2}{Mn}SO_4 + H_2O + \overset{0}{Cl_2}$$

- Determine the number of electrons gained and lost and equate them.

gain of $2e^- \times 1 = 2e^-$ (reduction)

$$Na\overset{-1}{Cl} + \overset{+4}{Mn}O_2 + H_2SO_4 \longrightarrow Na_2SO_4 + \overset{+2}{Mn}SO_4 + H_2O + \overset{0}{Cl_2}$$

loss of $1e^- \times 2 = 2e^-$ (oxidation)

- Use the multiplier obtained above to balance loss and gain of electrons

$$2NaCl + MnO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$$

- Balance the rest of equation by inspection method.

$$2NaCl + MnO_2 + 2H_2SO_4 \longrightarrow Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2$$

$$K_2Cr_2O_7 + HCl \longrightarrow KCl + CrCl_3 + H_2O + Cl_2$$

(Bahawalpur Board, 2011; Multan Board, 2012)

- Identify the elements, which undergo a change in oxidation number and write their oxidation numbers over the symbols.

$$K_2\overset{+6}{Cr_2}O_7 + H\overset{-1}{Cl} \longrightarrow KCl + \overset{+3}{Cr}Cl_3 + H_2O + \overset{0}{Cl_2}$$

- In this eq. Cl is oxidised from -1 in HCl to 0 in Cl_2. But it's oxidation state is not changed in KCl / or $CrCl_3$. Therefore, write HCl twice and determine the no. of electrons gained and lost and equate them.

gain of $2(3) = 6e^- \times 1 = 6e^-$ (reduction)

$$HCl + K_2\overset{+6}{Cr_2}O_7 + H\overset{-1}{Cl} \longrightarrow KCl + \overset{+3}{Cr}Cl_3 + H_2O + \overset{0}{Cl_2}$$

loss of $1e^- \times 6 = 6e^-$ (oxidation)

- Use the multiplier obtained above to balance loss and gain of electrons

$$HCl + K_2Cr_2O_7 + 6HCl \longrightarrow KCl + CrCl_3 + H_2O + Cl_2$$

- Balance the rest of equation by inspection method.

$$8HCl + K_2Cr_2O_7 + 6HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

Or

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

Q 6 (b) Balance the following equations by Ion-electron method

$Sn^{2+} + Fe^{3+} \longrightarrow Sn^{4+} + Fe^{2+}$ **(Sargodha Board, 2010)**

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$Fe^{3+} \longrightarrow Fe^{2+}$
$Sn^{2+} \longrightarrow Sn^{4+}$

- Write down the number of electrons gained and lost in each half reaction

$Fe^{3+} + 1e^- \longrightarrow Fe^{2+}$ (reduction half reaction) ____ (1)

$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$ (oxidation half reaction) ____ (2)

- Equate the total number of electrons gained and lost by multiplying eq.(1) by 2, and then add them.

$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$
$Sn^{2+} \longrightarrow Sn^{4+} + 2e^-$

$Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$

$H^+ + Cl^- + Cr_2O_7^{2-} \longrightarrow Cr^{3+} + Cl_2$

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$ (reduction half reaction)

$2Cl^- \longrightarrow Cl_2$ (oxidation half reaction)

- Balance oxygen by adding H_2O.

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$
$2Cl^- \longrightarrow Cl_2$

- Balance hydrogen by adding H^+ ions.

$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$

$2Cl^- \longrightarrow Cl_2$

- Write down the number of electrons gained and lost in each half reaction

$14H^+ + Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ ____ (1)

$2Cl^- \longrightarrow Cl_2 + 2e^-$ ____ (2)

- Equate the total number of electrons gained and lost by multiplying eq.(2) by 3. And then add the two half reactions.

$14H^+ + Cr_2O_7^{2-} + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

$6Cl^- \longrightarrow 3Cl_2 + 6e^-$

$Cr_2O_7^{2-} + 14H^+ + 6Cl^- \longrightarrow 2Cr^{3+} + 3Cl_2 + 7H_2O$

$Cu + NO_3^{-1} + H^+ \longrightarrow Cu^{2+} + NO_2 + H_2O$ **(Sargodha Board, 2010)**

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$NO_3^{-1} \longrightarrow NO_2$ (reduction half reaction)
$Cu \longrightarrow Cu^{2+}$ (oxidation half reaction)

- Balance oxygen by adding H_2O.

$NO_3^{-1} \longrightarrow NO_2 + H_2O$

$Cu \longrightarrow Cu^{2+}$

- Balance hydrogen by adding H^+ ions.

$2H^+ + NO_3^{-1} \longrightarrow NO_2$

$Cu \longrightarrow Cu^{2+}$

Write down the number of electrons gained and lost in each half reaction

$2H^+ + NO_3^{-1} + 1e^- \longrightarrow NO_2 + H_2O$ ____ (1)

$Cu \longrightarrow Cu^{2+} + 2e^-$ ____ (2)

- Equate the total number of electrons gained and lost by multiplying eq (1) by 2. And then add the two half reactions.

$4H^+ + 2NO_3^{-1} + 2e^- \longrightarrow 2NO_2 + 2H_2O$
$Cu \longrightarrow Cu^{2+} + 2e^-$

$2NO_3^{-1} + 4H^+ + Cu \longrightarrow Cu^{2+} + 2NO_2 + 2H_2O$

$$Cr_2O_7^{2-} + H_3AsO_3 \longrightarrow Cr^{3+} + H_3AsO_4$$

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} \quad \text{(reduction half reaction)}$$

$$H_3AsO_3 \longrightarrow H_3AsO_4 \quad \text{(oxidation half reaction)}$$

- Balance oxygen by adding H_2O.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$H_2O + H_3AsO_3 \longrightarrow H_3AsO_4$$

- Balance hydrogen by adding H^+ ions.

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$H_2O + H_3AsO_3 \longrightarrow H_3AsO_4 + 2H^+$$

- Write down the number of electrons gained and lost in each half reaction

$$14H^+ + 6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O \_\_\_\_ (1)$$

$$H_2O + H_3AsO_3 \longrightarrow H_3AsO_4 + 2e^- + 2H^+ \_\_\_\_ (2)$$

- Equate the total number of electrons gained and lost by multiplying eq.(2) by 3. And then add the two half reactions.

$$14H^+ + 6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$3H_2O + 3H_3AsO_3 \longrightarrow 3H_3AsO_4 + 6e^- + 6H^+$$

$$\overline{Cr_2O_7^{2-} + 8H^+ + 3H_3AsO_3 \longrightarrow 2Cr^{3+} + 3H_3AsO_4 + 4H_2O}$$

$$MnO_4^- + C_2O_4^{2-} \longrightarrow Mn^{2+} + CO_2$$ (Bahawalpur Board, 2011)

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$$MnO_4^- \longrightarrow Mn^{2+} \quad \text{(reduction half reaction)}$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 \quad \text{(oxidation half reaction)}$$

- Balance oxygen by adding H_2O.

$$MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

$$C_2O_4^{2-} \longrightarrow 2CO_2$$

- Balance hydrogen by adding H^+ ions.

$$8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O$$

$$C_2O_4^{2-} \longrightarrow 2CO_2$$

- Write down the number of electrons gained and lost in each half reaction

$$5e^- + 8H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4H_2O \_\_\_\_ (1)$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \_\_\_\_ (2)$$

- Equate the total number of electrons gained and lost by multiplying eq.(2) by 5 and eq.(1) by 2. And then add the two half reactions.

$$10e^- + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 8H_2O$$

$$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e^-$$

$$\overline{5C_2O_4^{2-} + 16H^+ + 2MnO_4^- \longrightarrow 2Mn^{2+} + 8H_2O + 10CO_2}$$

$$Fe^{2+} + Cr_2O_7^{2-} \longrightarrow Cr^{3+} + Fe^{3+}$$

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} \quad \text{(reduction half reaction)}$$

$$Fe^{2+} \longrightarrow Fe^{3+} \quad \text{(oxidation half reaction)}$$

- Balance oxygen by adding H_2O.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+}$$

- Balance hydrogen by adding H^+ ions.

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$Fe^{2+} \longrightarrow Fe^{3+}$$

- Write down the number of electrons gained and lost in each half reaction

$$14H^+ + 6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O \text{ \_\_\_\_ (1)}$$

$$Fe^{2+} \longrightarrow Fe^{3+} + 1e^- \text{ \_\_\_\_ (2)}$$

- Equate the total number of electrons gained and lost by multiplying eq.(2) by 6. And then add the two half reactions.

$$14H^+ + 6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^-$$

$$\overline{Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O}$$

$$IO_3^- + AsO_3^{3-} \longrightarrow I^- + AsO_4^{3-}$$

- Identify the elements, which undergo oxidation and reduction and split up the reaction, into oxidation and reduction half reactions.

$IO_3^- \longrightarrow I^-$ (reduction half reaction)

$AsO_3^{3-} \longrightarrow AsO_4^{3-}$ (oxidation half reaction)

- Balance oxygen by adding H_2O.

$$IO_3^- \longrightarrow I^- + 3H_2O$$

$$H_2O + AsO_3^{3-} \longrightarrow AsO_4^{3-}$$

- Balance hydrogen by adding H^+ ions.

$$6H^+ + IO_3^- \longrightarrow I^- + 3H_2O$$

$$H_2O + AsO_3^{3-} \longrightarrow AsO_4^{3-} + 2H^+$$

- Write down the number of electrons gained and lost in each half reaction

$$6e^- + 6H^+ + IO_3^- \longrightarrow I^- + 3H_2O \text{ \_\_\_\_ (1)}$$

$$H_2O + AsO_3^{3-} \longrightarrow AsO_4^{3-} + 2H^+ + 2e^- \text{ \_\_\_\_ (2)}$$

- Equate the total number of electrons gained and lost by multiplying eq.(2) by 3. and then add the two half reactions.

$$6e^- + 6H^+ + IO_3^- \longrightarrow I^- + 3H_2O$$

$$3H_2O + 3AsO_3^{3-} \longrightarrow 3AsO_4^{3-} + 6H^+ + 6e^-$$

$$\overline{IO_3^- + 3AsO_3^{3-} \longrightarrow 3AsO_4^{3-} + I^-}$$

$$Cr^{3+} + BiO_3^- \longrightarrow Cr_2O_7^{2-} + Bi^{3+}$$

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$BiO_3^- \longrightarrow Bi^{3+}$ (reduction half reaction)

$2Cr^{3+} \longrightarrow Cr_2O_7^{2-}$ (oxidation half reaction)

- Balance oxygen by adding H_2O.

$$BiO_3^- \longrightarrow Bi^{3+} + 3H_2O$$

$$7H_2O + 2Cr^{3+} \longrightarrow Cr_2O_7^{2-}$$

- Balance hydrogen by adding H^+ ions.

$$6H^+ + BiO_3^- \longrightarrow Bi^{3+} + 3H_2O$$
$$7H_2O + 2Cr^{3+} \longrightarrow Cr_2O_7^{2-} + 14H^+$$

- Write down the number of electrons gained and lost in each half reaction

$$2e^- + 6H^+ + BiO_3^- \longrightarrow Bi^{3+} + 3H_2O \text{ \_\_\_\_ (1)}$$

$$7H_2O + 2Cr^{3+} \longrightarrow Cr_2O_7^{2-} + 14H^+ + 6e^- \text{ \_\_\_\_ (2)}$$

- Equate the total number of electrons gained and lost by multiplying eq.(1) by 3. and then add the two half reactions.

$$6e^- + 18H^+ + 3BiO_3^- \longrightarrow 3Bi^{3+} + 9H_2O$$

$$7H_2O + 2Cr^{3+} \longrightarrow Cr_2O_7^{2-} + 14H^+ + 6e^-$$

$$\overline{3BiO_3^- + 2Cr^{3+} + 4H^+ \longrightarrow 3Bi^{3+} + Cr_2O_7^{2-} + 2H_2O}$$

$$OCl^- + S_2O_3^{2-} \longrightarrow Cl^- + S_4O_6^{2-}$$

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$$OCl^- \longrightarrow Cl^- \quad \text{(reduction half reaction)}$$

$$S_2O_3^{2-} \longrightarrow S_4O_6^{2-} \quad \text{(oxidation half reaction)}$$

- Balance oxygen by adding H_2O.

$$OCl^- \longrightarrow Cl^- + H_2O$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$$

- Balance hydrogen by adding H^+ ions.

$$OCl^- + 2H^+ \longrightarrow Cl^- + H_2O$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$$

- Write down the number of electrons gained and lost in each half reaction

$$2e^- + OCl^- + 2H^+ \longrightarrow Cl^- + H_2O \text{ ____ (1)}$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^- \text{ ____ (2)}$$

- Add the two half reactions.

$$2e^- + OCl^- + 2H^+ \longrightarrow Cl^- + H_2O$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^-$$

$$\overline{2S_2O_3^{2-} + OCl^- + 2H^+ \longrightarrow S_4O_6^{2-} + Cl^- + H_2O}$$

$$MnO_4^- + C_2O_4^{2-} \longrightarrow MnO_2 + CO_2$$

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$$MnO_4^- \longrightarrow MnO_2 \quad \text{(reduction half reaction)}$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 \quad \text{(oxidation half reaction)}$$

- Add two OH^- ions for one each oxygen atom on appropriate side.

$$MnO_4^- \longrightarrow MnO_2 + 4OH^-$$

$$C_2O_4^{2-} \longrightarrow 2CO_2$$

- Balance hydrogen by adding H_2O ions.

$$2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$$

$$C_2O_4^{2-} \longrightarrow 2CO_2$$

- Write down the number of electrons gained and lost in each half reaction

$$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^- \text{ ____ (1)}$$

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^- \text{ ____ (2)}$$

- Equate the total number of electrons gained and lost by multiplying eq.(1) by 2 and eq.(2) by 3. And then add the two half reactions.

$$6e^- + 4H_2O + 2MnO_4^- \longrightarrow 2MnO_2 + 8OH^-$$

$$3C_2O_4^{2-} \longrightarrow 6CO_2 + 6e^-$$

$$\overline{3C_2O_4^{2-} + 2MnO_4^- + 4H_2O \longrightarrow 2MnO_2 + 6CO_2 + 8OH^-}$$

$$MnO_4^- + CN^- \longrightarrow MnO_2 + CNO^-$$ *(D.G. Khan Board, 2009)*

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$$MnO_4^- \longrightarrow MnO_2 \quad \text{(reduction half reaction)}$$

$$CN^- \longrightarrow CNO^- \quad \text{(oxidation half reaction)}$$

- Balance hydrogen and oxygen by adding H_2O and OH^- ions.

$$2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^- \text{ ____ (1)}$$

$$CN^- + 2OH^- \longrightarrow CNO^- + H_2O \text{ ____ (2)}$$

- Write down the number of electrons gained and lost in each half reaction

$$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^- \text{ ____ (1)}$$

$$CN^- + 2OH^- \longrightarrow CNO^- + H_2O + 2e^- \text{ ____ (2)}$$

- Equate the total number of electrons gained and lost by multiplying eq.(2) by 3 and eq.(1) by 2, and then add the two half reactions.

$$6e^- + 4H_2O + 2MnO_4^- \longrightarrow 2MnO_2 + 8OH^- \_\_\_\_ (1)$$

$$3CN^- + 6OH^- \longrightarrow 3CNO^- + 3H_2O + 6e^- \_\_\_\_ (2)$$

$$3CN^- + H_2O + 2MnO_4^- \longrightarrow 2MnO_2 + 2OH^- + 3CNO^-$$

$$H_3AsO_3 + Cr_2O_7^{2-} \longrightarrow Cr^{3+} + H_3AsO_4$$

- Identify the elements, which undergo oxidation and reduction and split up the reaction into oxidation and reduction half reactions.

$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+}$ (reduction half reaction)

$H_3AsO_3 \longrightarrow H_3AsO_4$ (oxidation half reaction)

- Balance oxygen by adding H_2O.

$$Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$H_3AsO_3 + H_2O \longrightarrow H_3AsO_4$$

- Balance hydrogen by adding H^+ ions.

$$14H^+ + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2H^+$$

- Write down the number of electrons gained and lost in each half reaction

$$14H^+ + 6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O \_\_\_\_ (1)$$

$$H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2H^+ + 2e^- \_\_\_\_ (2)$$

- Equate the total number of electrons gained and lost by multiplying eq.(2) by 3. And then add the two half reactions.

$$14H^+ + 6e^- + Cr_2O_7^{2-} \longrightarrow 2Cr^{3+} + 7H_2O$$

$$3H_3AsO_3 + 3H_2O \longrightarrow 3H_3AsO_4 + 6H^+ + 6e^- \_\_\_\_ (2)$$

$$Cr_2O_7^{2-} + 8H^+ + 3H_3AsO_3 \longrightarrow 3H_3AsO_4 + 2Cr^{3+} + 4H_2O$$

HELLO! Mr. Question here!

Multiple Choice Questions from PAST PAPERS

1. Oxidation No. of oxygen in OF_2 is: (Lahore Board, 2014)
   (a) Zero (b) −1 / 2 (c) +2 (d) −1
2. The highest reduction potential in electrochemical is of F_2 and its value is (Rawalpindi Board, 2011)
   (a) −3.87V (b) −2.87V (c) +2.8V (d) +3.8V
3. The process during which one metal is deposited on the surface of an other metal by using electrical current is called (Rawalpindi Board, 2009, 2011)
   (a) Electrolysis (b) Electroplating
   (c) Delectrolytic refining (d) Electrolytic purification
4. Stronger the oxidizing agent, greater is the (Rawalpindi Board, 2010, 2013: Gujranwala Board, 2013, 2014)
   (a) oxidation potential (b) reduction potential
   (c) redox potential (d) E.M.F of cell
5. The electrolyte used in fuel cell is: (D.G. Khan Board, 2010: Lahore Board, 2009: D.G. Khan Board, 2010: Gujranwala Board, 2010)
   (a) aqueous NaCl (b) molten NaCl (c) KOH (d) $NaNO_3$
6. The oxidation number of chromium in $K_2Cr_2O_7$ is: (Rawalpindi Board, 2009: Gujranwala Board, 2009, 2010)
   (a) 14 (b) 12 (c) 6 (d) 13
7. Oxidation state of chromium in K_2CrO_4 is (Lahore Board, 2013)
   (a) 5 (b) 6 (c) 3 (d) 7
8. Nelson's cell and Down's cell are examples of (Gujranwala Board, 2008: Faisalabad Board, 2009)
   (a) electrochemical cell (b) galvanic cell (c) electrolytic cell (d) none of these
9. In reaction $3Fe + 3Cl_2 \rightarrow 2FeCl_3$: (Gujranwala Board, 2009)
   (a) Fe is reduced (b) Fe is oxidized (c) Cl_2 is oxidized (d) none of these
10. Galvanic cells which cannot be recharged are called: (Bahawalpur Board, 2009: Gujranwala Board, 2012)
    (a) diffused cells (b) secondary cells (c) tertiary cells (d) primary cells
11. In H_2O_2, the oxidation state of oxygen is: (Gujranwala Board, 2011)
    (a) +1 (b) −1 (c) +2 (d) −2
12. Electrode potential of SHE arbitrarily taken in volts is: (Gujranwala Board, 2011)
    (a) 0.00 (b) 1.00 (c) 0.01 (d) 0.50
13. Oxidation number of an element in free state is: (Multan Board, 2011)

(a) Zero (b) 1 (c) 2 (d) 3

14. The best oxidizing agent is: *(Multan Board, 2011)*
(a) F_2 (b) Cl_2 (c) Br_2 (d) I_2

15. Which process is used for the extraction of Al? *(Multan Board, 2013)*
(a) Castner-Kellner Process (b) Thermite Process
(c) Hall-Berouk Process (d) Combustion Process

16. An Oxidizing Agent: *(Multan Board, 2013)*
(a) Loses Electrons (b) Is Oxidized
(c) Neither gains nor loses electrons (d) Gains electrons

17. Oxidation Number of chromium in $Cr_2O_7^{-2}$ is (Rawalpindi Board, 2013)
(a) +3 (b) +4 (c) +5 (d) +6

18. Standard Hydrogen Electrode (SHE) is made of (Rawalpindi Board, 2013)
(a) Ag foil (b) Au foil (c) Cu foil (d) Pt foil

19. Stronger is the oxidizing agent greater is the. *(D.G. Khan Board, 2012)*
(a) oxidation potential (b) Reduction potential
(c) Redox potential (d) EMF of the cell

20. Oxidation number of oxygen in H_2O is *(Sargodha Board, 2009)*
(a) −2 (b) −1 (c) +1 (d) Zero

21. Oxidation number of chromium in K2CrO7 is *(Lahore Board, 2010)*
(a) 2 (b) 4 (c) 6 (d) 12

22. emf of Zn-Cu cell is *(Lahore Board, 2010)*
(a) 0.0 V (b) 0.5 V (c) 1.0 V (d) 1.1 V

23. The highest reduction potential in the electro chemical series is of F_2 and its value is: *(Faisalabad Board, 2010)*
(a) + 3.8 V (b) −3.87 V (c) −2.8 V (d) −2.87 V

24. The reaction $2K_2MnO_4 + Cl_2 \rightarrow 2KMnO_4 + 2KCl$ is: *(Faisalabad Board, 2010)*
(a) Chlorination of K_2MnO_4. (b) Neutralization reaction
(c) Oxidation reduction reaction (d) Neither oxidation nor reduction

25. In which of the following changes there is a transfer of five electrons? *(Multan board, 2010)*
(a) $MnO_4^{2-} \longrightarrow MnO_2$ (b) $MnO_4^{-1} \longrightarrow Mn^{2+}$
(c) $CrO_4^{2-} \longrightarrow Cr^{3+}$ (d) $CrO_7^{2-} \longrightarrow 2Cr^{+3}$

26. Electrolysis is the process in which a chemical reaction takes place at the expense of *(Multan board, 2010)*
(a) Chemical energy (b) electrical energy (c) urease (d) Invertase

27. In conversion of Br_2 to BrO_3^- the oxidation state of bromine changes from *(Sargodha Board, 2010)*
(a) 0 to −2 (b) 0 to −3 (c) 0 to 5 (d) 2 to 5

28. According to classical concept, oxidation involves *(Sargodha Board, 2010)*
(a) Addition of oxygen (b) removal of hydrogen
(c) Increase in oxidation state (d) all of above

29. Sulphur has highest oxidation state in *(Bahawalpur Board, 2010; Rawalpindi Board, 2010)*
(a) SO_3 (b) SO_2 (c) H_2S (d) H_2SO_3

30. Oxidation state of carbon in glucose is *(D.G. Khan Board, 2010)*
(a) zero (b) one (c) two (d) four

31. Which one is not an electrolyte *(Lahore Board, 2011)*
(a) Aqueous NaCl (b) Aqueous $CuSO_4$ (c) Cu metal (d) H_2SO_4

32. Oxidation state of Mn in MnO_4^{-2} is *(Lahore Board, 2011)*
(a) + 4 (b) + 6 (c) + 5 (d) − 6

33. Cathode in NICAD cell is *(Faisalabad Board, 2011)*
(a) Ag_2O (b) NiO_2 (c) Cd (d) Zn

34. Percentage of H_2SO_4 used in lead accumulator is *(Faisalabad Board, 2011)*
(a) 40% (b) 25% (c) 30% (d) 50%

35. Loss of electrons is called *(Lahore Board, 2007)*
(a) Oxidation (b) reduction (c) hydration (d) dehydration

36. Fuel cells convert chemical energy into *(Lahore Board, 2007)*
(a) Heat energy (b) Light energy (c) Electrical energy (d) Mechanical energy

37. The oxidation number of Mn in $KMnO_4$ is *(Faisalabad Board, 2007)*
(a) 3 (b) 5 (c) 7 (d) 9

38. If salt bridge is not used between two half cells, then the voltage *(Faisalabad Board, 2007)*
(a) decreases rapidly (b) decreases slowly
(c) does not change (d) drop to zero

39. In Na_2O_2, the oxidation state of oxygen is (Sargodha Board, 2011)
(a) − 2 (b) +2 (c) − 1 (d) +1

40. The oxidation state of carbon in $C_{12}H_{22}O_{11}$ *(Sargodha Board, 2013)*
(a) zero (b) − 6 (c) +6 (d) 12

Answers to Multiple Choice Questions from Past Papers.									
Q#	**Ans**	**Q#**	**Ans**	**Q#**	**Ans**	**Q#**	**Ans**	**Q#**	**Ans**
1	(c)	**2**	(c)	**3**	(b)	**4**	(a)	**5**	(c)
6	(c)	**7**	(b)	**8**	(c)	**9**	(b)	**10**	(d)
11	(b)	**12**	(a)	**13**	(a)	**14**	(a)	**15**	(c)
16	(a)	**17**	(d)	**18**	(d)	**19**	(b)	**20**	(a)
21	(c)	**22**	(c)	**23**	(d)	**24**	(c)	**25**	(b)
26	(b)	**27**	(c)	**28**	(d)	**29**	(a)	**30**	(a)
31	(c)	**32**	(b)	**33**	(b)	**34**	(c)	**35**	(a)
36	(c)	**37**	(c)	**38**	(d)	**39**	(c)	**40**	(a)

Detailed Explanation of Past Papers MCQs & Answers to all Past Papers SHORT QUESTONS In COLLEGE CHEMISTRY OBJECTIVE BOOK-I

SHORT & LONG QUESTIONS FROM PAST PAPERS

OXIDATION NUMBER, BALANCING OF EQUATION BY OXIDATION NUMBER AND ION ELECTRON METHODS

Short Questions

(1) Define electrochemistry. **(Faisalabad Board, 2008)**
(2) Define oxidation with an example. **(Gujranwala Board, 2011: Sargodha Board, 2012)**
(3) Define reduction. Give an example. **(Multan Board, 2007)**
(4) Differentiate between oxidation and reduction. **(Lahore Board, 2008: Faisalabad Board, 2008)**
(5) What are redox reactions? Give example. **(Gujranwala Board, 2012)**
(6) Define the oxidation number with an example. **(Sargodha Board, 2010)**
(7) Give Rules for oxidation Number of Hydrogen and Oxygen. **(Sargodha Board, 2011)**
(8) Prove that the oxidation number of some elements vary in different compounds **(Sargodha Board, 2007)**
(9) What is the oxidation state of Cl in $KClO$ and $KClO_3$ **(D.G. Khan Board, 2009)**
(10) Calculate the oxidation number of N in HNO_3 and NO_2 **(Faisalabad Board, 2011)**
(11) Calculate oxidation numbers of manganese in $KMnO_4$ and sulphur in SO_4^{2-}. **(Lahore Board, 2013)**
(12) Calculate the oxidation number of phosphorus in: **(Rawalpindi Board, 2013)**
(a) H_3PO_3 (b) Na_3PO_4

Long Questions

(1) Define oxidation number. Describe the rules used for the calculation of oxidation number of an element in molecules and ions. **(Rawalpindi board, 2007: Bahawalpur Board, 2009: Multan Board, 2013)**
(2) Give steps for balancing the Redox equation by Oxidation number method. **(Multan Board 2009)**

CONDUCTION, ELECTROLYSIS, ELECTROLTYIC PROCESS OF INDUSTRIAL PROCESS

Short Questions

(1) Define (a) electrolytic conduction (b) Electrolytic cell **(Lahore Board, 2009: Faisalabad Board, 2012: Sargodha Board, 2011)**
(2) Define electrolysis giving an example. **(Gujranwala Board, 2008: Faisalabad Board, 2009)**
(3) Differentiate between electrolysis and electrolytic conduction. **(Rawalpindi Board, 2011)**
(4) What will be the products and reactions of the electrolysis of molten (or fused) NaCl? **(Rawalpindi Board, 2009) (Gujranwala Board, 2013)**
(5) Write a brief note on electrolysis of aqueous solution of NaCl. **(D.G. Khan Board, 2012) OR** Write down cathodic and anodic reactions involved in electrolysis of aqueous solution of sodium chloride. **(D.G. Khan Board, 2007) OR** Give Cathodic and Anodic reactions of electrolysis of concentrated aqueous solution of Sodium Chloride. **(Multan Board, 2012)**
(6) Give two applications (or uses) of electrolysis processes of industrial importance. **(Bahawalpur Board, 2009: D.G. Khan Board, 2011: Multan Board, 2010, 2013)**
(7) What is the industrial importance of electrolysis? **(Sargodha Board, 2010)**

Long Questions

(1) Describe the electrolysis of molten NaCl and a concentrated solution of NaCl. **(Faisalabad Board, 2009: Gujranwala Board, 2009: Sargodha Board, 2013: Lahore Board, 2011)**
(2) Give the industrial importance of electrolysis process in detail? **(Gujranwala Board, 2010, 2014: Faisalabad Board, 2013)**

GALVANIC CELL, ELECTRODE POTENTIAL AND ITS MEASUREMENT, STANDARD HYDROGEN ELECTRODE

Short Questions

(1) What is standard electrode potential? Give example **(Faisalabad Board, 2008, 2010, 2012: D.G. Khan Board, 2009: Rawalpindi Board, 2011: Multan Board, 2008, 2012: Rawalpindi Board, 2013: Lahore Board, 2014: Gujranwala Board, 2014)**
(2) What is S.H.E.? Give its value. **(Bahawalpur Board, 2008)**
(3) OR What do you mean by standard hydrogen electrode (or SHE)? What is its use? OR What stands for, SHE? Define it. **(Sargodha Board, 2007: Faisalabad Board, 2009: Rawalpindi Board, 2009: Lahore Board, 2010)**
(4) State (or Differentiate) oxidation and reduction reactions. **(Bahawalpur Board, 2010: D.G. Khan Board, 2012)**
(13) How is Daniel cell (or Galvanic/Voltaic cell) represented **(Bahawalpur Board, 2010)**
(14) What is the function (or purpose) of salt bridge in galvanic cells? **(Bahawalpur Board, 2008: Lahore Board, 2009, 2013, 2014: Rawalpindi Board, 2010: Gujranwala Board, 2011, 2012, 2014: Sargodha Board, 2014) OR** What is salt bridge? **(Rawalpindi Board, Faisalabad Board, 2012, 2013: Sargodha Board, 2007)**
(15) How can we say that a voltaic cell is reversible cell? **(Lahore Board, 2007)**
(16) Why Zinc gives up (oxidizes) electrons and copper metal takes up them (reduces) in galvanic cell? **(Sargodha Board, 2009)**
(17) Write anodic and cathodic Reactions of Galvanic cell. **(Sargodha Board, 2011)**

Long Questions

(1) Describe the construction and working of standard hydrogen electrode. (Sargodha Board, 2009: Gujranwala Board, 2012: Lahore Board, 2013: Rawalpindi Board, 2014)

(2) How can you measure electrode potential of an element with the help of standard hydrogen electrode (SHE)? (Lahore Board, 2012) OR What is standard hydrogen electrode (SHE)? How it is used to measure the electrode potential of zinc? (Lahore Board, 2014) OR What is S.H.E.? Give the measurement of an unknown electrode potential with the help of it. (Bahawalpur Board, 2010)

(3) What is electrode potential. How electrode potential of Zn is measured? (Multan Board, 2011)

(4) Define electrode potential. Describe the construction of voltaic cell and reaction occurring in the cell. (Lahore Board, 2009) OR Describe a galvanic cell explaining the function of electrodes. (Rawalpindi Board, 2009)

ELECTROCHEMICAL SERIES AND ITS APPLICATIONS

Short Questions

(1) Define electrochemical series. Give its one application. (Bahawalpur Board, 2009; Lahore Board, 2007, 2013: Sargodha Board, 2013) NOTE: For one application see page

(2) How can we calculate voltage of a cell with the help of electrochemical series. Give example. (D.G. Khan Board, 2012)

(3) What is emf of a cell? (Multan Board, 2007)

(4) Write two applications of electro-chemical series. (Gujranwala Board, 2012)

(5) Describe the relative chemical reactivity of metals (Bahawalpur Board, 2011) OR How electrochemical series help us in determining the chemical reactivity of metals? (Gujranwala Board, 2013)

(6) Differentiate between oxidizing and reducing agent. (Gujranwala Board, 2008)

Long Questions

(1) What is electrochemical series? Also explain two/three applications of electrochemical series. (D.G. Khan board, 2007: Gujranwala Board, 2013: Sargodha Board, 2013)

PRIMARY AND SECONDARY CELLS

Short Questions

(1) Define primary cells and secondary cells (Sargodha Board, 2009)

(2) What are primary cells? Give example. (Multan Board, 2007)

(3) Differentiate between a primary and a secondary cell. (D.G. Khan Board, 2008: Multan Board, 2013)

(4) What is the difference between a cell and a battery? (Multan Board, 2009: Bahawalpur Board, 2010: D.G. Khan Board, 2010)

LEAD ACCUMULATOR, ALKALINE BATTERY, SILVER OXIDE BATTERY

Short Questions

(1) Give electrode reactions in lead storage battery. (Faisalabad Board, 2009, 2013)

(2) OR Describe redox reactions which occur during discharging of lead accumulator battery. (Sargodha Board, 2013: Multan Board, 2013)

(3) What is Lead Accumulator? Discuss in detail (Multan Board, 2010) OR Explain "Lead Accumulator" with charging and discharging. (D.G. Khan Board, 2011: Faisalabad Board, 2012)

(4) Describe the silver Oxide battery. OR Write a note on silver oxide battery. (Rawalpindi Board, 2012: Bahawalpur Board, 2012)

Long Questions

(1) Write down the reactions in alkaline battery. (Multan Board, 2008) OR What are electrode reactions of a dry cell? (Lahore Board, 2007)

NICKLE CADMIUM BATTERY, FUEL CELLS

Short Questions

(1) What is NICAD? (Gujranwala Board, 2010) OR Write down reactions taking place at the electrodes on the discharging of Nickle-Cadmium Cell. (Lahore Board, 2013)

(2) What is fuel cell and where it is used? (D.G. Khan Board, 2007: Rawalpindi Board, 2009)

(3) Give chemical reactions taking place at anode and cathode in a fuel cell. (Lahore Board, 2014)

(4) How power is generated by using the fuel cell? (Rawalpindi Board, 2007)

(5) Where are fuel cell used? How much fuel bond energy is converted into electricity in them? (Bahawalpur Board, 2008)

(6) Give some advantages of fuel cell. (Lahore Board, 2011)

Long Questions

(1) Describe Nickel Cadmium Cell (rechargeable). (Lahore Board, 2014)

(2) Write a note on the construction and working of fuel cells. (Azad Kashmir Board, 2012)

(3) Explain fuel cell with its construction, electrolytic reaction and diagram (Sargodha Board, 2014)

(4) Write comprehensive notes on alkaline battery and nickel-cadmium battery. (Bahawalpur Board, 2012)

TEST YOUR SKILLS

Marks: 85

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) If a substance is more easily oxidised than H atom, its E_{ox} is
(a) +ve (b) – ve (c) may be +ve or – ve (d) none

(ii) If electrode potential of $Zn/ZnSO_4$ is +0.76 volt. Its oxidation potential under same conditions will be
(a) 0.76V (b) > 0.76V (c) <0.76V (d) – 0.76V

(iii) Nelson's cell and Down's cell are examples of?
(a) electrochemical cell (b) galvanic cell (c) electrolytic cell (d) none of these

(iv) The oxidation number of 'Cl' in $Ca(ClO_3)_2$ is
(a) +3 (b) +5 (c) +1 (d) –1

(v) The cell will fuction if its calculated emf is
(a) +ve (b) – ve (c) either (d) zero

(vi) In Na_2O_2, the oxidation state of Oxygen is
(a) -2 (b) +2 (c) -1 (d) +1

(vii) Fuel cells usually operate at
(a) low temperature (b) high temperature
(c) moderate temperature (d) all temperature

(viii) A lead storage cell delivers
(a) 2V (b) 6V (c) 12V (d) depend upon the type

(ix) Electrolysis involves oxidation and reduction respectively at
(a) anode and cathode (b) cathode and anode
(c) at both electrodes (d) none of the electrodes

(x) Electrolysis is used for
(a) electroplating (b) manufacture of sodium metal (c) manufacture of Al (d) all of these

(xi) A cell in which chemical energy is converted into electrical energy is called
(a) electrolytic cell (b) galvanic cell (c) Down's cell (d) Nelson's cell

(xii) Electrolysis of aqueous solution of NaCl produces at anode
(a) H_2 gas (b) Cl_2 gas (c) NaOH (d) Na metal

(xiii) In conversion of Br_2 to Br_3^{-1}, the oxidation state of bromine changes from
(a) 0 to –2 (b) 0 to –3 (c) 0 to 5 (d) 2 to 5

(xiv) During electrolysis of aqueous solution of sodium nitrate, which ion is reduced at cathode
(a) H_3O^+ (b) Na^+ (c) OH^- (d) NO_3^-

(xv) The reduction potential of copper electrode is +0.34 V and that of Zn electrode is -0.76 V. When these two are coupled the emf of the cell is
(a) -0.42 V (b) +0.42 (c) -1.10 V (d) +1.10 V

(xvi) In which of the following compound, the oxidation state of hydrogen is -1
(a) H_2O (b) H_2O_2 (c) NaOH (d) NaH

(xvii) In the reaction $Cu + HNO_3 \rightarrow Cu(NO_3)_2 + NO + H_2O$, which of the following atom is oxidized
(a) Cu (b) H (c) N (d) O

SUBJECTIVE

Time: 2:10 Hours **Marks: 68**

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question numbers carefully. **(22x 2)=44**

Section – I

Q2. Answer any Eight parts from the followings.

(i) Write down the electrode reaction of silver oxide battery.

(ii) Zn can displace Cu from $CuSO_4$, but Cu can not displace Zn from $ZnSO_4$. Why?

(iii) Strong reducing agents have high values of standard reduction potential. Justify it.

(iv) What are the functions of salt bridge?

(v) What is anodized Al ?

(vi) Give one example of an electrolytic cell, in which electrodes also take part in reaction.

(vii) What is Hall and Beroult process?

(viii) How will you predict the feasibility of a chemical reaction?

(ix) How does electrochemical series tell us the distinction between oxidizing and reducing agents?

(x) Lead accumulator is a chargeable battery. justify it?

(xi) Differentiate between oxidation and reduction

(xii) What are primary cells? Give one example

Q3. Answer any Eight parts from the followings.

(i) SHE acts as anode when connected to Cu electrode but as cathode with Zn electrode. Explain with reason?

(ii) How does oxidation reduction reaction take place during electrolytic conduction?

(iii) What is industrial importance of electrolysis?

(iv) What are the products of electrolysis aqueous solution of NaCl. Give reactions?

(v) How copper is purified by an electrolytic cell?

(vi) How can a Galvanic cell be reversed?

(vii) What are cathode and anode?

(viii) What is SHE?

(ix) When Zn is coupled with SHE, then which reaction occurs at Zn electrode?

(x) Whether the reaction $Cu^{2+} + Zn$ $Cu + Zn^{2+}$ is spontaneous or not? Give reason?

(xi) What is meant by emf of a Galvanic cell?

(xii) Alkali metals (Li, Na, K and Rb) are highly reactive and coinage metals (Cu, Ag and Au) are least reactive. Why?

Q4. Answer any Six parts from the followings.

(i) Zn can liberate H_2 gas from acids but Cu can not. Why?

(ii) What are secondary cells?

(iii) Write down the electrode reactions in the lead accumulator?

(iv) Give Rules for oxidation Number of Hydrogen and Oxygen?

(v) Write anodic and cathodic reactions of Galvanic cell?

(vi) What is NICAD?

(vii) Name three chemicals which are used as fuels in fuel cells ?

(viii) What is meant by the term oxidation number or state of an element?

(ix) What is the oxidation state of Cr in $K_2Cr_2O_7$?

Section – II (Attempt any three questions) **(8x 3)=24**

Q5 (a) What is electrochemical series? Give its three applications. (04)
(b) What is standard hydrogen electrode? Give its construction and working. (04)

Q6 (a) Balance the following oxidation number method. (04)
(i) $Cu + HNO_3 \longrightarrow Cu(NO_3)_2 + NO_2 + H_2O$
(ii) $NaCl + H_2SO_4 + MnO_2 \longrightarrow Na_2SO_4 + MnSO_4 + H_2O + Cl_2$
(b) What are the advantages of fuel cells? (04)

Q7 (a) Balance the following equations by Ion electron method. (04)
(i) $CN^- + MnO_4^- \longrightarrow CNO^- + MnO_2$ (basic media)
(ii) $Cu + NO_3^{-1} \longrightarrow Cu^{+2} + 2NO_2$ (acidic media)
(b) Describe the process to determine the electrode potential using SHE. (04)

Q8 (a) What type of metals are more reactive? Explain with reference to electrochemical series. (03)
(b) How does a fuel cell generate electricity? (03)
(c) Determine the oxidation state of Cr in K_2CrO_4 and $Cr_2O_7^{2-}$ (02)

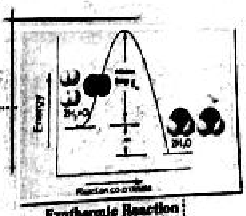
Q9 (a) Write down the rules for assigning oxidation states to elements in a compound. (04)
(b) Describe the construction and working of a Galvanic cell. (04)

Things to Remember

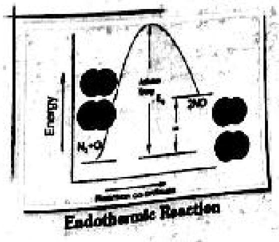
Chapter 11

REACTION KINETICS

Arrhenius

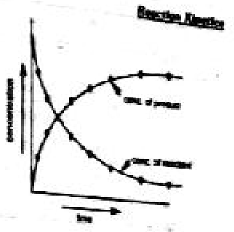


Exothermic Reaction



Endothermic Reaction

CONTENTS



INTRODUCTION

The branch of chemistry, which deals with the study of reaction rates and the factors, which affect these rates, is known as chemical kinetics or reaction kinetics.

Reaction kinetics helps to determine the mechanism of reactions.

TYPES OF CHEMICAL REACTIONS

On the basis of velocity of reactions, there are three types of reactions.

Slow Reactions

Some reactions occur very slowly and take even years to complete.

e.g. Consider the reaction

$$2H_2 + O_2 \longrightarrow 2H_2O$$

This reaction occurs very slowly and might take, perhaps, decades to complete.

Similar are the rusting of iron, chemical weathering of stone work of buildings by acidic gases in the atmosphere, fermentation of sugars etc.

Fast Reactions

Some reactions take almost no time to complete. Such reactions are fast reactions.

e.g. Consider the reaction

$$AgNO_{3(aq)} + NaCl_{(aq)} \longrightarrow NaNO_{3(aq)} + AgCl_{(s)}$$

This reaction is completed as soon as $AgNO_{3(aq)}$ and $NaCl_{(aq)}$ touches each other.

Moderate Reactions

Some reactions occur at moderate rates, neither too slow nor too fast.

e.g. Hydrolysis of ester

$$CH_3COOH + C_2H_5OH \longrightarrow CH_3COOC_2H_5 + H_2O$$

Multi Step Reactions

All reactions occur in <u>single step</u> or in <u>many steps</u>.

For <u>multistep</u> reactions, one of the step is <u>slow</u>. This is called rate determining step.

Other steps do not affect the rate of reaction.

RATE OF REACTION

It is the change in concentration of reactants or products divided by the time taken for the change

$$\text{Rate} = \frac{\text{Change in conc. of the substance}}{\text{Time taken for change}} = \frac{\Delta c}{\Delta t}$$

During a chemical reaction, reactants are converted into products.

As the reaction proceeds, the concentration of reactant decreases with time and the concentration of product increases with time. Therefore, rate of reaction can be defined as

The rate of decrease in concentration of reactants

or ***The rate of increase in concentration of products.***

Explanation

When reaction starts, concentration of reactants decreases with time, while concentration of product increases. At start, rate of reaction is generally very fast. Thus, the slope of curve is steepest for both reactants and products as shown in the fig.

After some time, the slope becomes less steep showing that reaction rate decreases with time. It shows that rate of a reaction is changing at every moment.

Actually, rate of reaction is decreasing with time. It never remains uniform during different time period. It decreases continuously until the reaction stops.

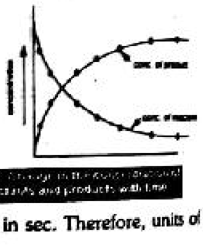


Figure: Change in the concentration of reactants and products with time

Units

Usually, concentrations are expressed in mol dm^{-3} and time in sec. Therefore, units of rate are

$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{\text{mol/dm}^3}{\text{sec}} = \text{mol dm}^{-3}\ \text{sec}^{-1}$$

For gaseous reactions, partial pressures of gases are used instead of molar concentrations.

INSTANTANEOUS AND AVERAGE RATE

AVERAGE RATE

The rate of a reaction between specific time intervals is called the average rate of reaction.

Let amount of product formed at t_1 is c_1 and at t_2 is c_2, then

$$\text{Average rate} = \frac{c_2 - c_1}{t_2 - t_1} = \frac{\Delta c}{\Delta t}$$

INSTANTANEOUS RATE

The rate at any one instant during the interval is called instantaneous rate.

Let 'x' is the amount of product produced at any time 't' then instantaneous rate can be expressed as

$$\text{Instantaneous Rate} = \frac{dx}{dt}$$

The dx/dt (differential of x w.r.t. 't') is called rate of change of conc. w.r.t. time i.e. it represents instantaneous reaction rate.

dx and dt are very small changes in concentration and time respectively.

For a general reaction

$$A \longrightarrow B$$

The rate of reaction can be expressed in terms of rate of disappearance of A or rate of appearance of B i.e.

$$\text{Rate} = -\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

Where 'd [A]' and 'd [B]' are very small change in concentrations of A and B respectively.

Negative sign indicates that conc. of A decreases with time, while

Positive sign indicates that conc. of B increases with time.

Relationship between Instantaneous and Average Rates

- At start, instantaneous rate is greater than average rate
- At the end of the interval, the instantaneous rate becomes less than average rate.
- When the time interval approaches zero, average and instantaneous rates become equal.
- Average and instantaneous rates become equal for only one instant during the interval.

Rate Constant or Velocity Constant

Rate constant is the rate of reaction when the concentrations of reactants are unity

- It is denoted by 'k'
- Under give conditions, k remains constant.
- It changes with temperature.

Explanation

According to the law of Mass Action

Rate of a chemical reaction is directly proportional to the product of active masses of reactants involved in the chemical reaction.

Thus for a simple reaction

$aA + bB \longrightarrow$ products

Rate = $k[A]^a[B]^b$

Where k = specific rate constant

When $[A]=[B]=1\ mol/dm^3$ then

Rate = k

Thus, *Rate constant is the rate of reaction when the concentrations of reactants are unity*

ORDER OF REACTION

The number of reacting molecules whose concentration changes during a reaction is called order of reaction

Consider a general reaction

$aA + bB \longrightarrow$ products

Rate equation for this reaction will be

Rate of reaction = $k[A]^a[B]^b$

a is the order of reaction w.r.t A

b is the order of reaction w.r.t B

The sum a + b is called overall order of reaction

Thus, order of reaction can be defined as

The sum of the powers to which concentrations are raised in the rate law expression is called order of reaction

Order of a reaction is an experimental quantity. It cannot be determined by reaction equation.

In chemical kinetics, reactions are classified as zero order, first order, second order and third order.

Zero Order Reaction

When the reaction is independent of the concentration of reactants, it is called zero order reaction.

Examples

Decomposition of HI (on gold surface)

$2HI \xrightarrow{\text{on gold surface}} H_2 + I_2$

The experimental rate equation for this reaction is

Rate = $k[HI]^0 = k$

This reaction is independent of the concentration of HI, hence it is a zero order reaction.

Photochemical reactions are usually zero order.

First Order Reactions

When sum of powers to which concentrations are raised in the rate law expression is equal to 1.

Examples

1. Decomposition of nitrogen pentoxide.

$N_2O_{5\,(g)} \longrightarrow N_2O_{4\,(g)} + \frac{1}{2}O_{2\,(g)}$

The experimental rate equation for this reaction is

Rate = $k[N_2O_5]$

Hence it is first order w.r.t. the concentration of N_2O_5.

2. Hydrolysis of tertiary butyl bromide (*Pseudo First Order reaction*)

The reactions in which rate depend upon only one molecule although more than one molecules are involved is called a pseudo first order reaction.

tertiary butyl bromide tertiary butyl alcohol

The experimental rate equation for this reaction is

Rate = $k[(CH_3)_3CBr]$

Hence, it is first order w.r.t. $(CH_3)_3CBr$. The rate of reaction is independent of the concentration of water because, it is present in very large excess. Thus, it is a pseudo first order reactions.

Second Order Reactions

When sum of powers to which concentrations are raised in the rate law expression is equal to 2.

Example

Oxidation of nitric oxide with ozone

$NO_{(g)} + O_{3\,(g)} \longrightarrow NO_{2\,(g)} + O_{2\,(g)}$

The experimental rate equation for this reaction is

Rate = $k[NO][O_3]$

This reaction is first order w.r.t. NO and first order w.r.t. O_3. The sum of the individual orders is equal to two. Hence it is a second order reaction.

Third Order Reactions

When sum of powers to which concentrations are raised in the rate law expression is equal to 3

<u>Example</u>

<u>Reaction of $FeCl_3$ with KI</u>

$$2FeCl_{3(aq)} + 6KI_{(aq)} \longrightarrow 2FeI_{2(aq)} + 6KCl_{(aq)} + I_2$$

This reaction involves eight reactant molecules. However, the experimental rate equation for this reaction is

$$Rate = k\,[FeCl_3]\,[KI]^2$$

This reaction is first order w.r.t. $FeCl_3$ and second order w.r.t. KI.

The sum of the individual orders is equal to three. Hence it is a third order reaction.

It shows that it is a multistep reaction and one step is the rate determining step. The possible steps are

$$FeCl_{3(aq)} + 2KI_{(aq)} \xrightarrow{slow} FeI_{2(aq)} + 2KCl_{(aq)} + Cl^-_{(aq)}$$

$$2KI_{(aq)} + 2Cl^-_{(aq)} \xrightarrow{fast} 2KCl_{(aq)} + I_{2(s)}$$

NOTE:

The order of a reaction is usually positive integer or a zero, but it can also be in fraction or can have a negative value.

<u>Example: Formation of Carbon Tetrachloride Form Chloroform.</u>

$$CHCl_{3(l)} + Cl_{2(g)} \longrightarrow CCl_{4(l)} + HCl_{(g)}$$

The experimental rate equation for this reaction is

$$Rate = k\,[CHCl_3][Cl_2]^{1/2}$$

The sum of exponents will be $1 + ½ = 1.5$

Hence the order of this reaction is 1.5.

RATE LAW

The experimental relationship between a reaction rate and the concentration of the reactants is known as the rate law or the rate equation for that reaction.

Consider a general reaction

$$aA + bB \longrightarrow Products$$

Rate eq. for this reaction will be

$$Rate = k[A]^a[B]^b$$

'a' and 'b' are determined experimentally. Rate law expression is, therefore, an experimental expression.

HALF-LIFE PERIOD OR HALF LIFE TIME

The time required to convert 50% of the reactants into products is called half life of the reaction.

It is denoted by $t_{1/2}$ or $t_{0.5}$

<u>Example 1: Decomopoaition of N_2O_5</u>

$$2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$

Half life period for decomposition of N_2O_5 is 24 minutes at 45°C

It means that if reaction is started with 0.1 mol/dm³ of N_2O_5 then after 24 minutes, 0.05 mole/dm³ will be left behind.

Similarly, after 48 minutes <u>(two half life periods)</u>, 0.025 mol/dm³(25%) will be left behind and after 72 minutes <u>(three half life periods)</u>, 0.0125 mol/dm³(12.5%) will be left behind.

Decomposition of N_2O_5 is a first order reaction.

Above experiment clearly shows that <u>half life time of a first order reaction is independent of the initial concentration of reactants</u>.

<u>Example 2: Disintegration of</u> $^{235}_{92}U$

It has a half life period of <u>7.1×10^8</u> years or <u>710 million</u> years. It is also a first order reaction.

It means that if 1 kg of $^{235}_{92}U$ is present, then after 710 million years, 0.5 kg is converted into daughter elements, and in the next 710 years, 0.25 kg of the $^{235}_{92}U$ will be consumed.

Relationship between Half Life and Order of Reaction

Generally,

Half life period is inversely proportional to initial concentration of reactants raised to the power one less than the order of reaction.

$$(t_{1/2})_n \propto \frac{1}{a^{n-1}}$$

Where n = Order of reaction a = Initial conc. of reactants

$(t_{1/2})_n$ = Half life period for n^{th} order reaction.

- For first order reaction, half life period is independent of the initial concentration of reactants.

  i.e $(t_{1/2})_1 \propto \frac{1}{a^0}$, since $(t_{1/2})_1 = \frac{0.693}{k}$

- For a second order reaction, half life period is inversely proportional to the initial concentration of reactants.

  i.e $(t_{1/2})_2 \propto \frac{1}{a^1}$, since $(t_{1/2})_2 = \frac{1}{ka}$

- For a third order reaction, half life period is inversely proportional to the square of initial concentration of reactants.

  i.e $(t_{1/2})_3 \propto \frac{1}{a^2}$, since $(t_{1/2})_3 = \frac{1.5}{ka^2}$

  Hence half-life period can be used to determine the order of reaction.

Example 1

Calculate the half-life period of the following reaction when the initial conc. is 0.05 M

$$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$$

$$k = 0.079\ dm^3\ mol^{-1}\ s^{-1} \text{ at } 508^\circ C \text{ and Rate} = k[HI]^2$$

Solution:

$k = 0.079\ dm^3\ mol^{-1}\ s^{-1}$

concentration of HI = a = 0.05 M

Since the reaction is second order, therefore

For a second order reaction

$$(t_{1/2})_2 = \frac{1}{k \times a^{2-1}} = \frac{1}{k \times a}$$

$$(t_{1/2})_2 = \frac{1}{0.079 \times 0.050} = \boxed{253\ sec}$$

Exercise Q11.

The rate determining step of a reaction is found out from mechanism of that reaction. Explain it with few examples. *(Take second example on **page 643**: $2NO + 2H_2 \rightarrow 2H_2O + N_2$)*

RATE DETERMINING STEP

The reaction, which determines the overall rate of reaction, is called rate-determining step.

For multistep reaction, rate determining step is the slowest step.

Explanation

Reactions may occur in single step or several steps. The reactions, which occur in more than one steps, are called multistep reactions.

For a single step reaction, the only step is always the rate determining step.

For multistep reactions, One of the step is slowest. This is called rate determining step. Other steps do not affect the rate of reaction.

The total number of reactant molecules that takes part in rate determining step appear in the experimental rate equations of reaction.

Hence, experimental rate equations can give information about mechanism of reactions.

Example 1:

$$NO_{2(g)} + CO_{(g)} \longrightarrow NO_{(g)} + CO_{2(g)}$$

The experimental rate equation for this reaction is

$$\text{Rate} = k[NO_2]^2$$

This rate equation shows that, rate is independent of concentration of CO. Thus, it shows that it is a multistep reaction. Moreover, one step is slow which is the rate-determining step and involves two molecules of NO_2.

Thus, following mechanism can be written

$$NO_2 + NO_2 \xrightarrow{slow} NO_3 + NO$$

$$NO_3 + CO \xrightarrow{fast} NO_2 + CO_2$$

So, first step is slow and it is the rate determining step.

NO_3 is not produced in the reaction. It is consumed as soon as it is formed. Such a specie is called reaction intermediate.

Reaction Intermediate

The specie which produce only for short period of time during a reaction is called reaction intermediate.

Reaction intermediate is unstable as compared to both reactants and products. In some cases, under certain conditions, it may be stable and can be isolated.

Exercise Q10:

A curve is obtained when graph is plotted between time on x-axis and concentration on y-axis. The measurement of the slopes of various points gives us the instantaneous rates of reaction. Explain with suitable examples.

DETERMINATION OF THE RATE OF CHEMICAL REACTIONS

While measuring rate of reaction, progress of reaction is noted either by physical methods or chemical methods. In these methods, conc. of one of the reactant or product is determined at different time intervals.

The different concentrations obtained are then plotted against the time. The slope of curve at any time 't' on conc-time graph will give the Rate of Reaction at that time.

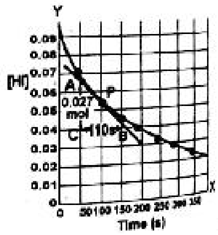
Table Change in concentration of HI with regular intervals

$2HI(g) \rightarrow H_2(g) + I_2(g)$

Concentration of HI (mol dm⁻³)	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300
0.0265	350

The slope at any point on the graph (e.g., at point P) can be obtained by drawing tangent to the curve at that point. A right angle triangle ABC is completed with tangent as hypotenuse, such that

$$\text{Rate of reaction} = \frac{AC}{BC} = \frac{\Delta C}{\Delta t}$$



Example

Consider the decomposition HI to H_2 and I_2 at 508 °C.

The conc. of HI determined at various times is given in the table

This table clearly shows that for first 50 sec, the decrease in conc. of HI is 0.0284 mol/dm³, while between 300 to 350 sec, the decrease is only 0.0031 mol/dm³.

Hence, rate is faster at the start, but slower at the end.

It has also shown by the slope of graph. Graph shows that slope is greater at the beginning than at the end. And greater the slope higher is the rate.

The rate of this reaction at any time can be determined by drawing tangent to the graph at the required time. Slope of the tangent will give the rate at that time.

e.g. at point P,

$$\text{slope} = \text{rate} = \frac{0.027}{110} = 2.5\times10^{-4} \text{ moles dm}^{-3}\text{s}^{-1}$$

- The right angled triangle can be of any size, same rate of reaction will be obtained
- If a graph is plotted with concentration of H_2 or I_2, a rising curve will be obtained. However, the rate at any time will be the same as with graph of HI.

EXPERIMENTAL TECHNIQUES FOR MEASURING RATE OF REACTION

Physical Methods

In physical methods, progress of reaction is noted, by observing the changes in physical properties of the reaction mixture.

Most commonly used physical methods are

(i) Spectrometry (ii) Conductometry (iii) Dilatometric method
(iv) Refractrometry (v) Polarimetry

Spectrometry

This technique is used if reactant or product absorb UV/VIS or IR light

The amount of radiation absorbed is directly proportional to the progress of reaction.

Conductometry

This method is best for ionic reactions. Each ion has its own conductivity. When ions are formed or consumed during a reaction, then conductivity changes. Hence, progress of reaction can be noted by measuring the conductivity changes.

The conductivity change is directly proportional to the rate of change in concentration of the ions.

Dilatometric method

This method is used for reactions in which volume is changed.

The volume change is directly proportional to the progress of reaction.

Refractrometry

This method is used for reactions in solution, in which refractive indices of substances change.

The change in refractive index is directly proportional to the progress of reaction

Optical Rotation Method (Polarimetry)

This method is used when one of the substances is optically active. i.e. it can rotate the plane polarized light. The angle of rotation is determined by polarimeter.

The change in angle of rotation is directly proportional to the progress of reaction.

After measurement, graph is plotted and rate of reaction is determined from the graph.

Chemical Methods

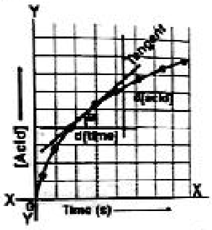
In these methods, samples are withdrawn from reaction vessel at different time intervals. These samples are then analyzed chemically in order to determine the concentration of one of the reactants or products at different times.

Example

Consider the hydrolysis of ethyl acetate

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

During this reaction samples are taken out of reaction vessel at different times and placed into about four times of its volume in ice cold water to stop the reaction. The dilution and chilling stop the reaction. The concentration of CH_3COOH produced in the reaction is noted every time by titrating against standard alkali solution using phenolphthalein as indicator.



The different concentrations of acetic acid are plotted against the time. A rising curve is obtained. Initially rate of reaction is high but it decreases with time. The rate is determined from the concentration–time graph. When the curve becomes horizontal, the rate becomes zero.

If curve is plotted with concentrations of reactant, then a falling curve is obtained.

> It is a pseudo first order reaction. Since water is present in large excess as compare to ester, therefore, it does not affect the rate of reaction.

ENERGY OF ACTIVATION

The minimum amount of energy which molecules must have, in addition to their average K.E., to form an activated complex, is called the Activation Energy.

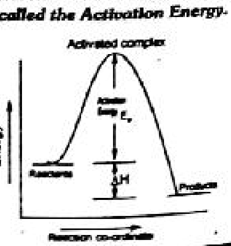
It is denoted by E_a

Units: It is expressed in joules

Explanation

In a reaction system, molecules constantly collide with one another.

At ordinary temperature, activation energy is usually very high for any reaction system. Therefore, most of the molecules



reaction and the potential energy of the reaction

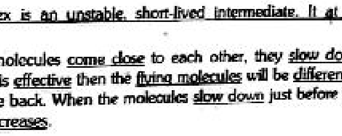
simply rebound after collisions and do not form activated complex.

However, if some of the molecules gain enough energy after collisions to form activated complex, they will start the reaction. Such collisions, which form an activated complex are called effective collisions. For effective collisions, molecules must have proper orientation.

If all the collisions are effective then the reaction will be completed soon. However, most of the reactions are slow showing that all collisions are not effective.

The number of effective collisions increases with increase in temperature and thus rate of reaction is also increased and vice versa.

Colliding molecules first form a high energy transition state or activated complex, which then leads to product. It can be represented as



Activated complex is an unstable, short-lived intermediate. It at once changes into product.

When colliding molecules come close to each other, they slow down, collide and fly apart. If the collision is effective then the flying molecules will be different, if not, then same molecules will bounce back. When the molecules slow down just before collision, their K.E. decreases and P.E. increases.

Relationship Between ΔH And Ea

The heat of reaction is equal to the difference of potential energy between reactants and products.

Exothermic reaction

For exothermic reactions, energy of reactant is higher than the energy of product. The difference of energy is released as heat. The decrease in P.E. of the reactants appear as increase in K.E. of the products.

It has been shown in the fig.

Endothermic reactions

For endothermic reactions, energy of reactant is lower than the energy of product. The difference of energy is absorbed as heat. For such reactions, a continuous supply of energy is needed.

It has been shown in the fig.

It is clear that, both for exothermic and endothermic reactions, there is energy barrier, which must be overcome in order to start the reaction.

For all reactions, activation energy is different for forward and backward reactions. For exothermic reaction, E_a is less for forward reaction than backward reaction. And for endothermic reaction, E_a is more for forward than backward reaction. E_a give information about mechanism of reaction.

Exothermic Reaction

FINDING THE ORDER OF REACTION

Many methods are used to determine the order of reaction.

- Hit and Trial method
- Graphical method
- Differential method
- Half life method
- Method of large excess

Half-life method

Half life period is inversely proportional to initial concentration of reactants raised to the power one less than the order of reaction.

$$(t_{1/2})_n \propto \frac{1}{a^{n-1}}$$

Where n = Order of reaction

a = Initial conc. of reactants

$(t_{1/2})_n$ = Half life period for n^{th} order reaction.

Let a reaction is carried out with two different initial concentration of reactants a_1 and a_2. Let two half-life times are t_1 and t_2 respectively.

Then

$$t_1 \propto \frac{1}{a_1^{n-1}} \text{ ——— (1)} \quad \text{and} \quad t_2 \propto \frac{1}{a_2^{n-1}} \text{ ——— (2)}$$

Divide eq. (1) by (2)

$$\frac{t_1}{t_2} = \frac{1/a_1^{n-1}}{1/a_2^{n-1}} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking log on both sides

$$\log\left(\frac{t_1}{t_2}\right) = \log\left(\frac{a_2}{a_1}\right)^{n-1}$$

or $$\log\left(\frac{t_1}{t_2}\right) = (n-1)\log\left(\frac{a_2}{a_1}\right)$$

$$\frac{\log\left(\frac{t_1}{t_2}\right)}{\log\left(\frac{a_2}{a_1}\right)} = (n-1)$$

or $$n = 1 + \frac{\log\left(\frac{t_1}{t_2}\right)}{\log\left(\frac{a_2}{a_1}\right)}$$

Thus knowing t_1 and t_2 at a_1 and a_2 , order of reaction 'n' can be determined.

Example 2

In the thermal decomposition of N_2O at 760°C, the time required to decompose half of the reactant was 255 sec. at the initial P of 290 mm Hg and 212 sec at the initial P of 360 mm Hg. Find the order of this reaction.

Solution:

For 1^{st} experiment

Initial conc. = a_1 = 290 mm

Half life time = t_1 = 255 sec.

For 2^{nd} experiment

Initial conc. = a_2 = 360 mm

Half life time = t_2 = 212 sec.

Order of reaction is given by

$$n = 1 + \frac{\log\left(\frac{t_1}{t_2}\right)}{\log\left(\frac{a_2}{a_1}\right)}$$

$$\text{or} \qquad n = 1 + \frac{\log\left(\frac{255}{212}\right)}{\log\left(\frac{360}{290}\right)}$$

$$\text{or} \qquad n = 1 + \frac{0.0802}{0.0940} = \boxed{1.85 \approx 2}$$

Hence, it is a second order reaction

Method of Large Excess

In this method, one of the reactants is taken in small amount while others are taken in large amounts.

Since conc. of reactants present in large amount is almost constant. Therefore, rate does not depend on their concentrations.

Hence rate only depends upon the conc. of reactant taken in small amount. It is because small changes in its amount greatly affect the rate. Thus order of reaction w.r.t. this reactant is determined.

Similarly, this process is repeated with all the reactants by taking them in small amounts.

Thus order of reaction w.r.t. each reactant is determined.

Hence overall order of reaction is the sum of the orders w.r.t. each reactant.

Exercise Q12:
Discuss the factors influencing the rates of chemical reaction.

FACTORS AFFECTING RATE OF REACTIONS

Following factors affect the reaction rates

1. Nature of reactant
2. Concentration of reactants
3. Surface Area
4. Light
5. Temperature
6. Catalyst

(1) NATURE OF THE REACTANT

Reaction rates are greatly affected by the nature of Reactant.

The reactivity of a substance is controlled by its electronic arrangement.

Examples

- Elements of group I-A reacts more rapidly with H_2O than elements of group II-A.
- Neutralization and double decomposition reactions are very fast.
- Ionic reactions are very fast e.g. reaction between HCl and NaOH is completed in just 10^{-6} sec, at room temperature.
- Redox reactions involve transfer of electrons, therefore, these are slower than ionic reactions.

(2) EFFECT OF CONCENTRATION

Rate of reaction is affected by changing concentration in accordance with law of Mass Action. This law states

"The rate at which a substance reacts, is directly proportional to its active mass, and the rate of reaction is directly proportional to the product of active masses of reacting substances".

Thus by increasing conc. of any reactant, rate of reaction is increased and by decreasing conc. rate of reaction is decreased.

The frequency of collisions between molecules depends upon their concentrations. The more crowded the molecules, the more chance of collision. Hence, rate of reaction increases.

Examples

- Combustion in normal air (with 21 % O_2) becomes faster in pure O_2
- Lime stone reacts with different rate with different concentration of HCl
- Concentration of gases can be increased by increasing their pressure and hence rate of reaction increases.

Exercise Q13.
Explain the following facts about the reaction.

$$2NO + 2H_2 \rightarrow 2H_2O + N_2$$

(i) The changing concentrations of reactants change the rates of this reaction.
(ii) Individual orders with respect to NO and H_2 can be measured.
(iii) The overall orders can be evaluated by keeping the concentration of one of the substances constant.

Consider the reaction

$$2H_2 + 2NO \longrightarrow 2H_2O + N_2$$

Experimental data for this reaction is given below

Table (11.2) Effect of change in concentrations of reactants on the rate of reaction

[NO] in (moles dm^{-3})	$[H_2]$ in (moles dm^{-3})	Initial rate (atm min^{-1})
0.006	0.001	0.025
0.006	0.002	0.050
0.006	0.003	0.075
0.001	0.009	0.0063
0.002	0.009	0.025
0.003	0.009	0.056

Experiments show that by keeping concentration of NO constant, and doubling the concentration of H_2, double the reaction rate and tripling the concentration of H_2 triples the rate.

Thus, rate of reaction depends on the first power of concentration of H_2

i.e. Rate α $[H_2]$ ____ (1)

Similarly, keeping concentration of H_2 constant and doubling concentration of NO raises the rate to 4 times, and tripling concentration of NO, raises the rate to 9 times.

Thus, rate of reaction depends on square of concentration of NO

i.e. Rate α $[NO]^2$ ____ (2)

Combining (1) and (2)

Rate α $[H_2][NO]^2$

Rate = $k[H_2][NO]^2$

It's the rate law for the given reaction. It shows that it is a third order reaction. Thus, rate equation for this reaction is not according to balanced equation.

To satisfy rate eq. following mechanism can be proposed

$$2NO + H_2 \xrightarrow{slow} N_2 + H_2O_2 \text{ (rate determining step)}$$

$$H_2O_2 + H_2 \xrightarrow{fast} 2H_2O$$

(3) SURFACE AREA

By increasing surface area, contact between reacting molecules increases. Hence rate of reaction increases.

Example

- Al foil reacts slowly with NaOH but powdered Al reacts rapidly with cold NaOH

$$2Al + 2NaOH + 6H_2O \longrightarrow 2NaAl(OH)_4 + 3H_2$$

- $CaCO_3$ in big pieces react slowly with H_2SO_4, but it reacts rapidly in powdered form.

(4) LIGHT

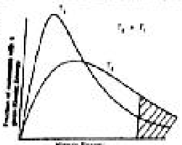
Light consists of photons of definite energies. When light is given to a reaction, its energy increases the rate of reaction

Examples

- Reaction of CH_4 and Cl_2 requires light
- Reaction of H_2 and Cl_2 is negligible in darkness, slow in day light but explosive in sunlight.
- Photosynthesis requires light.
- Reactions of silver halide in photography requires light.

(5) Effect of Temperature

According to collision theory, rate of reaction is proportional to the number of collisions among the molecules. Thus, if frequency of collisions is increased, rate of reaction is also increased. However, all the collisions do not result in reaction. Only effective collisions can give activation energy to the molecules.



To start reaction, molecules must gain activation energy E_a

At low temperature mostly molecules posses average energy and only small fraction of molecules posses necessary E_a for reaction as shown in the fig by shaded area. Most of the molecules possess average energy.

With increase in temperature, the fraction of molecules with high energy increases. The curve at higher temperature T_2 has flattened. Thus, there is wider distribution of velocities. At higher temperature T_2, number of molecule having high energy increases while number of molecules with low energy decreases. Thus, effective collisions will be increased and the rate of reaction will also be increased.

When the temperature is raised by 10 K, the fraction of molecules with energy more than E_a roughly doubles. Thus, the rate of reaction is also doubled.

Q15. *How does Arrhenius equation help us to calculate the energy of activation of reaction?*

Arrhenius Equation (Effect of T)

Increase in T increases the rate of reaction and vice versa.

Generally, rate of reaction doubles for every 10°C rise in temperature.

Effect of temperature on reaction rate is best explained by Arrhenius equation.

$k = Ae^{-E_a/RT}$ ____ (1)

Where k= rate constant

A = Frequency factor or Arrhenius constant

e = Base of natural logarithm. Its value is 2.718281

E_a = Energy of Activation

R = General gas constant

T = Absolute temperature

'A' depends upon the collision frequency of the reactants.

Taking natural log of eq (1)

$$\ell n k = \ell n A - \frac{E_a}{RT} \ell n e$$

Since ℓn e = 1 and ℓn = 2.303 log , therefore

$$2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$$

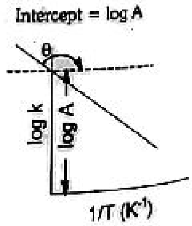
Divide throughout by 2.303

$$\log k = \log A - \frac{E_a}{2.303RT} \quad \text{\_\_ (2)}$$

This equation shows that

- <u>Higher the activation energy, lower will be rate constant</u>
- <u>Higher the temperature, higher will be the rate constant</u>

Intercept = log A



Calculation of Activation Energy

Eq (2) is an equation of straight line.

i.e. y = −mx + c

Where 'm' = slope of line

'c' = intercept of straight line

A <u>graph</u> between <u>log k</u> and $\frac{1}{T}$, will give a <u>straight line</u> with

$$\text{Slope} = \frac{-E_a}{2.303R} \quad \text{and intercept} = \log A$$

$$\text{Thus Slope} = \frac{-E_a}{2.303R}$$

$$\text{or } E_a = -\text{slope} \times 2.303 \times R$$

- Slope is determined by measuring <u>tangent of angle 'θ'</u>. Angle 'θ' is obtained by drawing a line <u>parallel to x – axis</u> and measure angle 'θ'. Take tan θ, which is the slope.
- <u>Different reactions</u> will have different straight lines and <u>different slopes</u>.

Units of Slope:

$$\text{Slope} = \frac{-E_a}{2.303R} = \frac{J\,mole^{-1}}{2.303J\,mole^{-1}K^{-1}} = K$$

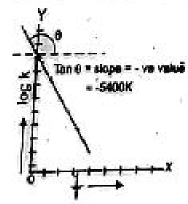
Example 3

A plot of Arrhenius eq. for the thermal decomposition of N_2O_5 is shown in the following fig. The slope is found to be −5400 K. Calculate the energy of activation of this reaction.

Solution:

Arrhenius eq. is

$$\log k = \log A - \frac{E_a}{2.303RT}$$



From Arrhenius eq.

$$\text{slope} = -\frac{E_a}{2.303R}$$

or $E_a = -\ 2.303 \times R \times \text{slope}$

$E_a = -\ 2.303 \times 8.314 \times (-5400)$

$E_a = 103394.57\ J = \boxed{103.39\ kJ\ mol^{-1}}$

This shows that the thermal decomposition of N_2O_4 requires 103.39 kJ mol^{-1} energy in addition to the average energy of reactant to cross the energy barrier.

(6) Catalyst

A substance that changes the rate of reaction without being consumed in the reaction is called catalyst.

A catalyst increases the rate of reaction by decreasing the activation energy of the reaction.

Example

- Reaction between H_2 and O_2 is very slow at room temperature. However, it speeds up in the presence of Pt catalyst.

CATALYSIS

Catalyst

A substance that changes the rate of reaction but remains chemically unchanged at the end of reaction is called catalyst.

Function Of Catalyst

A catalyst lowers the activation energy of the reaction by providing a different way for reaction as shown in the fig.

By lowering E_a, more molecules can easily cross the energy barrier and hence reaction rate increases.

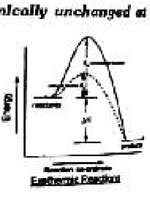


Fig [illegible] Catalyzed and uncatalyzed reactions

Example

- Reaction between H_2 and O_2 is very slow at room T. But it speeds up in the presence of Pt catalyst.
- $KClO_3$ decomposes much more rapidly in the presence of a small amount of MnO_2
- HCl is oxidized to Cl_2 in the presence of $CuCl_2$.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

CATALYSIS

The process, which takes place in the presence of a catalyst, is called catalysis.

A catalyst gives a new reaction path with low activation energy.

Thus more molecules can cross the new energy barrier and reaction rate increases.

Types of Catalysis

(1) Homogeneous Catalysis

(2) Heterogeneous Catalysis

(1) Homogeneous Catalysis

In this process, the catalyst and the reactants are in the same phase.

The reacting system is homogeneous throughout and the catalyst is distributed uniformly through the system.

Examples:

1. Oxidation of SO_2 to SO_3 in the lead chamber process for the manufacture of sulphuric acid, needs NO as a catalyst.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO} 2SO_{3(g)}$$

Both the reactants and the catalyst are gases.

2. Esters are hydrolysed in the presence of H_2SO_4.

Both the reactants and the catalyst are in the solution state.

$$CH_3COOC_2H_{5(aq)} + H_2O_{(l)} \xrightleftharpoons{H^+} CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

(2) Heterogeneous Catalysis

In this process, the catalyst and the reactants are in different phases.

Mostly the catalyst is in the solid phase, while the reactants are in the gaseous or liquid phase.

Examples:

1. Oxidation of ammonia to NO is carried out in the presence of platinum gauze during manufacturing of HNO_3.

$$4NH_{3(g)} + 5O_{2(g)} \xrightleftharpoons{Pt} 4NO_{(g)} + 6H_2O_{(g)}$$

2. Hydrogenation of unsaturated organic compounds are catalysed by finely divided Ni

$$CH_2 = CH_{2(g)} + H_{2(g)} \xrightarrow{Ni} CH_3 - CH_{3(g)}$$

3. Oxidation of SO_2 to SO_3 in the contact process for the manufacture of sulphuric acid, needs V_2O_5 as a catalyst.

$$2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)}$$

CHARACTERISTICS OF A CATALYST

A catalyst is not changed in mass and chemical composition at the end of reaction.

1. Its physical state may be changed.

e.g. For the decomposition of $KClO_3$, MnO_2 is added in the form of granules. It is converted to fine powder at the end of reaction.

In many cases shining surfaces of the solid catalyst become dull.

2. Sometimes only a trace of a metal catalyst is used to affect very large amount of reactants.

Examples

- 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water.
- Dry HCl and NH_3 combine in the presence of trace of moisture to give dense white fumes of NH_4Cl.
- Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.

3. A catalyst is more effective in finely divided form. It is because increase in surface area increases the efficiency of a catalyst and rate of reaction increases.
   e.g. a big piece of Pt have much less catalytic activity than colloidal Pt.
   In the hydrogenation of vegetable oils finely divided nickel is used.
4. A catalyst cannot affect the equilibrium constant of a reaction. It only decrease the time to reach equilibrium.
5. A catalyst cannot start a reaction, which is not thermodynamically feasible.
6. The mechanism of a catalysed reaction is different from that of an uncatalysed reaction.
7. **Specificity:** A catalyst is specific in its action. A particular catalyst works for one reaction. It may not work for any other reaction.
8. If different catalysts are used for the same reactant then the products may change.
   Examples
   Formic acid is decomposed by Al_2O_3 to water and CO while Cu decomposes it to H_2 to CO_2.
   $$HCOOH \xrightarrow{Al_2O_3} H_2O + CO$$
   $$HCOOH \xrightarrow{Cu} H_2 + CO_2$$
9. **Effect of Temperature:** Temperature affects the role of a catalyst.
   Physical state of some catalyst is changed by change in T, Hence their catalytic power will be decreased. e.g. colloidal catalysts like platinum may be coagulated with the rise in temperature.
10. **Poisoning of a Catalyst:** Catalyst may be poisoned by trace amounts of other substances. Thus they become ineffective. Such substances are called poisons.
    The poisoning of a catalyst may be temporary or permanent.
    In permanent poisoning, the poison reacts chemically with the catalyst.
    Example: Compounds of sulphur and arsenic act as poisons to many metallic catalysts. e.g. Pt

Examples

(i) Decomposition of H_2O_2 is catalysed by colloidal platinum. Pt can be made ineffective by traces of HCl.
(ii) In Haber's process, presence of CO as an impurity with hydrogen decreases the catalytic activity of catalyst.
(iii) In Contact process of manufacturing of H_2SO_4, Pt is used as a catalyst. Traces of arsenic as impurity in the reacting gases makes Pt ineffective. That's why arsenic purifier is used in the contact process.

Activation of Catalyst or Promoters

A substance, which promotes the activity of a catalyst, is called a promoter or activator.

It is also called "catalyst for a catalyst".

Examples:

i) Hydrogenation of vegetable oils is carried out by Ni.
   The catalytic activity of Ni can be increased by using Cu and tellurium.
ii) In Haber's process for the manufacture of ammonia, iron is used as a catalyst. If small amounts of some high melting oxides like aluminium oxide, chromium oxide or rare earth oxides are added, the efficiency of iron is increased.

NEGATIVE CATALYST

A substance, which decreases the rate of reaction, is called a negative catalyst or inhibitor.

Example

Tetraethyl lead is added to petrol, because it saves the petrol from pre-ignition.

AUTOCATALYST

In some of the reactions, a product formed may act as a catalyst. This phenomenon is called auto-catalysis.

Examples

1. Hydrolysis of ethyl acetate generates acetic acid, which acts as a catalyst for further reaction.
2. When copper is allowed to react with nitric acid, the reaction is slow in the

beginning. It gains speed slowly and finally becomes very fast.

This is due to the formation of nitrous acid during the reaction, which speeds up the process.

3. The reaction of oxalic acid with acidified $KMnO_4$ is slow at the beginning but $MnSO_4$ produced in the reaction makes it faster.

$$2KMnO_4 + 3H_2SO_4 + 5(COOH)_2 \xrightarrow{Mn^{2+}} K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

Exercise Q18:
What are enzymes? Give examples in which they act as catalyst. Mention the characteristics of enzyme catalysis?

ENZYME CATALYSIS

Enzyme are the complex protein molecules and catalyze the organic reactions in the living cells. They are called biochemical catalysts.

Many enzymes have been identified and obtained in the pure crystalline state. The first enzyme was prepared in the laboratory in 1969.

Examples:

1. Urea undergoes hydrolysis into NH_3 and CO_2 in the presence of enzyme urease present in soyabean.

$$\underset{\text{urea}}{H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + H_2O \xrightarrow{\text{urease}} 2NH_3 + CO_2$$

2. Glucose is converted into ethanol by zymase enzyme present in the yeast.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

3. Concentrated sugar solution undergoes hydrolysis into glucose and fructose by invertase enzyme, present in the yeast.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} C_6H_{12}O_6 + C_6H_{12}O_6$$

Mode of Enzyme Action

Enzymes have <u>active centres</u> or cavities on their <u>surfaces</u>. The molecules of a substance fit into cavities, form complex, reacts and the product is get out of the cavity immediately.

<u>Michaulis and Menter</u> proposed following mechanism for enzyme catalysis

<u>Step – I</u>

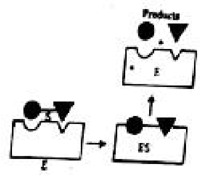
$$E + S \rightleftharpoons ES$$

E = Enzyme, S = Substrate ES=Complex

<u>Step – 2</u>

$$ES \longrightarrow P + E$$

(P=Product)



Characteristics of Enzymes Catalysis

The role of enzymes as catalyst is like inorganic heterogeneous catalysts. They are highly efficient and specific.

1. <u>Enzymes are the most efficient catalysts known</u> and they lower the energy of activation of a reaction.
2. <u>Enzyme catalysis is highly specific</u>
   e.g. <u>urease</u> catalyses the hydrolysis of urea only and it cannot hydrolyse any other amide even methyl urea.
3. Enzyme catalytic reactions have maximum rates at an optimum temperature.
4. The <u>pH of the medium</u> also controls the rates of the enzyme catalysed reactions.
   Each enzyme has an optimum pH.
5. The activity of enzyme is greatly enhanced by the presence of a co-enzyme or activator.

OBJECTIVE AND SHORT ANSWER QUESTIONS (Exercise)

Q1. Multiple choice questions.

(i) In zero order reaction, the rate is independent of

(a) Temperature of reaction (b) Concentration of reactants.
(c) Concentration of products (d) None of these

(D.G. Khan Board, 2009) (Multan Board, 2011, 2012)

(ii) If the rate equation of a reaction 2A + B → Products is, Rate= $k[A]^2[B]$, and A is present in large excess. Then order of reaction is

(a) 1 (b) 2 (c) 3 (d) none of these

(Sargodha Board, 2009) (Rawalpindi Board, 2012)

(iii) The rate of reaction

(a) Increases as the reaction proceeds.
(b) Decreases as the reaction proceeds.
(c) Remains the same as the reaction proceeds.
(d) May decreases or increase as the reaction proceeds.

(Rawalpindi Board, 2009) (D.G. Khan Board, 2012)

(iv) With increases of 10°C temperature, the rate of reaction doubles. This increase in rate of reaction is due to:

(a) Decrease in activation energy of reaction.
(b) Decrease in the number of collisions between reactant molecules.
(c) Increase in activation energy of reactants.
(d) Increase in number of effective collisions.

(v) The unit of the rate constant is the same as that of the rate of reaction in

(a) First order reaction. (b) Second order reaction.
(c) Zero order reaction. (d) Third order reaction.

(Faisalabad Board, 2009) (Bahawalpur Board, 2009) (Multan Board, 2011) (Sargodha Board, 2011, 2012) (D.G. Khan Board, 2012) (Lahore Board, 2013) (Gujranwala Board, 2011, 2012, 2013, 2014)

ANSWERS TO MULTIPLE CHOICE QUESTIONS

(i) Ans: (b)

Consider a reaction

A → Products

If this reaction is a zero order reaction then its rate equation is given as

Rate = $k[A]^0 = k$

It means that the rate of reaction is independent of the concentration of reactant.

(ii) Ans: (a)

When a reactant is taken in large excess, its conc. is not changed during reaction and remains almost constant. Therefore, rate of reaction does not depend upon the conc. of such reactant.

Since A is in excess, therefore, rate will depend upon conc. of B only. Hence, it will be a first order reaction.

i.e. Rate = $k'[B]$

(iii) Ans: (b)

According to the law of mass action, rate of a reaction is directly proportional to the product of concentrations of reactants. As the reaction proceeds, the concentration of reactants decreases. Hence, rate of reaction also decreases.

(iv) Ans: (d)

According to the collision theory, rate of reaction depends upon the number of collisions among reactant molecules. With increase in temperature, the number of collisions among reactant molecules also increases. Hence, rate of reaction doubles.

(v) Ans: (c)

Consider a reaction

A → Products

If this reaction is a zero order reaction, then its rate equation is given as

Rate = $k[A]^0 = k$

Hence units of 'k' is the same as that for rate of reaction. i.e. mol $dm^{-3}s^{-1}$

Q2. Fill in the blanks with suitable words.

(i) The rate of endothermic reaction ____ with the increase in temperature.
(ii) All radioactive disintegration reactions are of ____ order
(iii) For a fast reaction the rate constant is relatively ____ and half-life is ____.
(iv) The second order reaction becomes ____ if one of the reactants is in large excess.
(v) Arrhenius equation can be used to find out ____ of a reaction.

Answers:
(i) increases (ii) first (iii) greater, short
(iv) first order (v) energy of activation

Q3. Indicate TRUE or FALSE as the case may be.

(i) The half life of a first order reaction Increases with temperature.
(ii) The reactions having zero activation energies are instantaneous.
(iii) A catalyst makes a reaction more exothermic.
(iv) There is no difference between rate law and the law of mass action.
(v) The order of reaction is strictly determined by the stoichiometry of the balanced equation.

Answers:
(i) False (ii) True (iii) False (iv) False (v) False

Q4 *What is chemical kinetics? How do you compare chemical kinetics with chemical equilibrium and thermodynamics?*

Chemical kinetics

- It is the study of rates of reactions and the factors, which affects these rates like concentration, temperature, catalyst etc.
- It gives information about mechanism of reactions.
- Both reversible and irreversible reactions are studied in chemical kinetics.

Chemical equilibrium

- It is the state of a reversible reaction at which the rate of forward reaction becomes equal to the rate of reverse reaction.
- It is only concerned with reversible reactions.
- Le-chatlier's principle is used to study the effects temperature, pressure and concentration on equilibrium state.

Thermodynamics

- It is the study of energy changes.
- It tells about the feasibility of a chemical reaction.

Q5. *The rate of chemical reaction with respect to products is written with positive sign, but with respect to reactants is written with negative sign. Explain it with reference to the following hypothetical reaction.*

$$aA + bB \rightarrow cC + dD$$

During a chemical reaction, reactants are converted into products and their concentrations change. Thus, rate of a reaction can be expressed with respect to any reactant or product.

However, as the reaction proceeds, the concentration of reactants decreases with time and the concentration of products increases with time. Thus, rate of chemical reaction with respect to products is written with positive sign but with respect to reactants, it is written with negative sign.

Hence, rate of above hypothetical reaction can be expressed as

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$

Q6. *What are the instantaneous rates and average rates? Is it true that instantaneous rate and rate of a reaction at the beginning of reaction is greater than the average rate and becomes far less than average rate near the completion of reaction?*

The rate of reaction between specific time intervals is called the average rate of reaction.
While

The rate at any one instant during the interval is called instantaneous rate.

Q7 *Differentiate between*

(i) Rate and Rate constant of a reaction

	Rate of a reaction		Rate constant of a reaction
1	It is the change in concentration of reactants or products divided by the time taken for the change.	1	It is the rate of a reaction when the concentration of reactants are unity.
2	It changes with time.	2	It does not changes with time.
3	It depends upon the concentration of reactants.	3	It is independent of the concentration of reactants.
4	It is a variable quantity.	4	It is a constant quantity.
5	Its units are mol $dm^{-3}s^{-1}$	5	Its unit depends upon the order of reaction.
6	**Example:** Consider a general reaction $A + B \rightarrow C + D$ Its rate is given as Rate = k[C][D], where 'k' is the rate constant.		

(ii) Homogenous catalysis and Heterogenous catalysis
(Sargodha Board, 2011; Rawalpindi Board, 2013; Gujranwala Board, 2014)

	Homogenous catalysis		Heterogeneous catalysis
1	In this catalysis, reactants and catalyst are in the same phase.	1	In this catalysis, reactants and catalyst are in the different phase.
2	In this, the system remains homogenous during the reaction.	2	In this, the system remains heterogeneous during the reaction.
3	Mostly liquids and gases are used as homogeneous catalysts.	3	Mostly solid are used as heterogeneous catalysts.
4	Example: $2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{NO} 2SO_{3(g)}$ NO is homogeneous catalyst	4	Example: $2SO_{2(g)} + O_{2(g)} \xrightleftharpoons{V_2O_5} 2SO_{3(g)}$ V_2O_5 is heterogeneous catalyst

Q8. Justify the following statements

(i) The rate of a chemical reaction is an ever changing parameter under the given conditions. *(Sargodha Board, 2011: Multan Board, 2012,*

OR What happens to the rate of a chemical reaction with the passage of time? *(Multan Board, 2011: Lahore Board, 2013)*

According to the law of mass action, rate of a chemical reaction is directly proportional to the concentration of reactants.

When the reaction starts, the concentration of reactants is high, therefore, rate of reaction is fast. As the concentration of reactants is decreased, the rate of a reaction is also decreased. At the end of reaction, the reaction becomes very slow. Hence, rate of a chemical reaction is an ever changing parameter.

(ii) The reaction rate decreases every moment but the rate constant 'k' of the reaction is a constant quantity, under the given conditions. Justify it.

According to the law of mass action, rate of a chemical reaction is directly proportional to the concentration of reactants.

Consider a general reaction

$$A + B \rightarrow C + D$$

Its rate is given as

Rate = k[A][B], where 'k' is the rate constant.

As the reaction proceeds, concentration of reactants is decreased, therefore, rate is also decreased. However, rate constant 'k' is not changed. It is proportionality constant.

(iii) 50% of a hypothetical first order reaction completes in one hour. The remaining 50% needs more than one hour to convert itself into products.

The time required for half of the reactants (i.e. 50%) to convert into products is called half life time of the reaction. For a first order reaction, half life time is a constant quantity under given conditions.

For the above hypothetical first order reaction, half life time is one hour. Therefore, if we start with 100% reactants then the reaction will proceed as

Time (hour)	0	1	2	3	4
Amount of reactant	100	50	25	12.5	6.75

Hence, after every one hour, amount of reactant becomes half.

It shows that 50% of the reactants are consumed in one hour. In next hour, 50% of the remaining amount is consumed. Thus in a total of two hours, 75% of the total amount is consumed.

Hence, 50% reactants are consumed in one hour but the remaining 50% will take many hours to be consumed.

(iv) The radioactive decay is always a first order reaction. *(Rawalpindi Board, 2007: D.G. Khan Board, 2007: Lahore Board, 2007: Faisalabad Board, 2009: Sargodha Board, 2009: Gujranwala Board, 2011, 2012, 2014: Sargodha Board, 2007, 2012: Multan Board, 2012)*

The rate of radioactive decay depends on the amount of radioactive substance. Since only one substance (reactant) is involved in this process, therefore, it is always a first order reaction. Moreover, the half-life time for the radioactive decay of a particular substance is also constant. Hence, it is a first order process.

(v) The units of rate constant of second order reaction is $dm^3 mol^{-1} s^{-1}$ but the unit of rate of reaction is $mol\ dm^{-3} s^{-1}$.

Rate of reaction is the change in concentration with change in time. Therefore, its units are given as

$$\text{Rate} = \frac{\Delta c}{\Delta t} = \frac{mol/dm^3}{sec} = mol\ dm^{-3}\ sec^{-1}$$

However, for a second order reaction the rate of reaction is directly proportional to the concentration of two reactants e.g., A and B. i.e.

Rate = k[A][B], where 'k' is the rate constant.

$$\text{Or} \quad k = \frac{\text{Rate}}{[A][B]}$$

Since the units of rate = mol dm^{-3} sec^{-1}, and concentration of A and B are expressed in mol dm^{-3}, therefore, units of k will be

$$k = \frac{\text{Rate}}{[A][B]} = \frac{mol\ dm^{-3} s^{-1}}{mol\ dm^{-3} \times mol\ dm^{-3}} = dm^{3} mol^{-1} s^{-1}$$

(vi) The sum of the co-efficients of a balanced chemical equation is not necessarily important to give the order of reaction. *(Gujranwala Board, 2009: Sargodha Board, 2009: Multan Board, 2012)*

A balanced chemical equation only gives the stoichiometry of the reaction. It does not deal with the mechanism of the reaction. However, order of reaction is determined experimentally and it depends upon the mechanism of reaction. Actually, it depends upon the slow step of the reaction. Therefore, the co-efficients in balanced chemical equation has no relation with order of reaction. e.g., consider the reaction

$$2H_2 + 2NO \rightarrow 2H_2O + N_2$$

Rate of this reaction is

Rate = $k[H_2][NO]^2$

Hence, its order is 1+2=3 (third order reaction)

Sum of co-efficients in balanced chemical equation = 2+2=4.

However, the sum of co-efficient may be equal to the order of reaction.

Sometimes, the sum of co-efficient may be equal to the order of reaction.

(vii) The order of a reaction is obtained from the rate expression of a reaction and the rate expression is obtained from the experiments.

Order of reaction depends upon the mechanism of reaction. Actually, it depends upon

the slow step of the reaction, which controls the overall rate of reaction.

Consider a general reaction

$$A + B \rightarrow C + D$$

Rate expression for this reaction will be

$$\text{Rate} = k[A]^a[B]^b,$$

'a' and 'b' indicates the number of molecules involved in the slow step of the reaction. These are determined experimentally. Rate expression is, therefore, an experimental expression. Hence, order of reaction (i.e. a+b) is also an experimental quantity.

Q9. *Explain that half life time method for measurement of the order of a reaction can help us to measure the order of even those reactions which have a fractional order.*

Using half life method, order of reaction can be determined by the equation

$$n = 1 + \frac{\log\left(\frac{t_1}{t_2}\right)}{\log\left(\frac{a2}{a1}\right)}$$

where n=order of reaction

t_1 is the half life time when the concentration of reactants is a_1, and t_2 is the half life time when the concentration of reactants is a_2.

Thus knowing t_1 and t_2 at a_1 and a_2 respectively, order of reaction 'n' can be determined. The answer can be in whole number or in fraction. Hence, half life time method can be used to determine both simple and fractional order.

Q10. *A curve is obtained when graph is plotted between time on x-axis and concentration on y-axis. The measurement of the slopes of various points gives us the instantaneous rates of reaction. Explain with suitable examples.*

Solved on Page 636

Q11. *The rate determining step of a reaction is found out from mechanism of the reaction. Explain it with few examples.*

Solved on Page 635

Q12. *Discuss the factors influencing the rates of chemical reaction.*

Solved on Page 642

Q13. *Explain the following facts about the reaction.*

$$2NO + 2H_2 \rightarrow 2H_2O + N_2$$

(i) The changing concentrations of reactants change the rates of this reaction.

(ii) Individual orders with respect to NO and H_2 can be measured.

(iii). The overall orders can be evaluated by keeping the concentration of one of the substances constant.

Solved on Page 643

Q14. *The collision frequency and the proper orientation of molecules are necessary conditions for determining the proper rate of reaction. Justify the statement.*

Solved on Page 638

Q15. *How does Arrhenius equation help us to calculate the energy of activation of reaction?*

Solved on Page 645

Q16. *Define the following terms and give examples.*

(i) Homogeneous catalysis	*Solved on Page 649*
(ii) Heterogeneous catalysis	*Solved on Page 649*
(iii) Activation of a catalyst	*Solved on Page 651*
(iv) Auto catalysis	*Solved on Page 651*
(v) Catalytic poisoning	*Solved on Page 650*
(vi) Enzyme catalysis	*Solved on Page 652*

Q17. *Briefly describe the following with examples*

(i) Change of physical state of a catalyst at the end of reaction.

The physical state of a catalyst may be changed at the end of reaction.

Example 1: For the decomposition of $KClO_3$, MnO_2 is added in the form of granules. It is converted to fine powder at the end of reaction.

Example 2: In many cases shining surfaces of the solid catalyst become dull.

(ii) A very small amount of a catalyst may prove sufficient to carry out a reaction.

Sometimes only a trace of a metal catalyst is used to affect very large amount of reactants.

Example 1: 1 mg of fine platinum powder can convert 2.5 dm^3 of H_2 and 1.25 dm^3 of O_2 to water.

Example 2: Thousands of dm^3 of H_2O_2 can be decomposed in the presence of 1 g of colloidal platinum.

(iii) A finely divided catalyst may prove more effective.

A catalyst is more effective in finely divided form. It is because increase in surface area increases the efficiency of a catalyst and rate of reaction increases.

Example 1: e.g. a big piece of Pt have much less catalytic activity than colloidal Pt.

Example 2: In the hydrogenation of vegetable oils finely divided nickel is used.

(iv) Equilibrium constant of a reversible reaction is not changed in the presence of a catalyst.

A catalyst cannot affect the equilibrium constant of a reaction. It only decrease the time to reach equilibrium.

Example: $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

In this reaction, few drops of H_2SO_4 are used as catalyst. So, the equilibrium is established within hours. However, if catalyst is not used then it may take days to reach the equilibrium. In both cases, the equilibrium constant will be same at same temperature.

(v) A catalyst is specific in its action. (Sargodha Board, 2007; Lahore Board, 2009)

OR A particular catalyst is suitable for a particular reaction. Justify it. (Multan Board, 2008; Faisalabad Board, 2011)

A catalyst is specific in its action. A particular catalyst works for one reaction. It may not work for any other reaction.

Example:

Urease enzyme catalyses the hydrolysis of urea only and it cannot hydrolyse any other amide even methyl urea.

$$\underset{\text{urea}}{H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + H_2O \xrightarrow{\text{urease}} 2NH_3 + CO_2$$

Q18. What are enzymes? Give examples in which they act as catalyst. Mention the characteristics of enzyme catalysis?

Solved on Page 652

IMPORTANT FROMULAS

Determination of order of reaction by half life method: $n = 1 + \dfrac{\log\left(\dfrac{t_1}{t_2}\right)}{\log\left(\dfrac{a2}{a1}\right)}$

Arrhenius equation to determine activation energy:

$\log k = \log A - \dfrac{E_a}{2.303RT}$ **or** $k = Ae^{-Ea/RT}$

$\text{slope} = -\dfrac{E_a}{2.303R}$ **or** $E_a = -2.303 \times R \times \text{slope}$

NUMERICAL PROBLEMS (Exercise)

Q19. In the reaction of NO and H_2, it was observed that equimolecular mixture of gases at 340.5 mm pressure was half changed in 102 seconds. In another experiment with an initial pressure of 288 mm of Hg, the reaction was half completed in 140 seconds. Calculate the order of reaction.

Solution:

For 1^{st} experiment

Initial concentration $= a_1 = 340.5$ mm

Half life time $= t_1 = 102$ sec.

For 2^{nd} experiment

Initial concentration $= a_2 = 288$ mm

Half life time $= t_2 = 140$ sec.

Order of reaction is given by

$$n = 1 + \frac{\log\left(\frac{t_1}{t_2}\right)}{\log\left(\frac{a2}{a1}\right)}$$

or $$n = 1 + \frac{\log\left(\frac{102}{140}\right)}{\log\left(\frac{288}{340.5}\right)}$$

or $$n = 1 + \frac{-0.1375}{-0.0727}$$

$$n = 1 + \frac{0.1375}{0.0727} = \boxed{1.89 = 3}$$

Hence, it is a third order reaction

Q.20. A study of chemical kinetics of a reaction

$$A + B \longrightarrow \text{products}$$

Gave the following data at 25°C. Calculate the rate law

Exp. No.	[A]	[B]	Rate
1	1	0.15	4.2×10^{-6}
2	2	0.15	8.4×10^{-6}
3	1	0.2	5.6×10^{-6}

Solution:

Comparison of Exp. (1) and (2) shows that keeping [B] constant and doubling [A], doubles the reaction rate

Thus Rate α $[A]^1$

Comparison of Exp. (1) and (3) shows that keeping [A] constant and changing [B] from 0.15 to 0.2, rate changes from 4.2×10^{-6} to 5.6×10^{-6}

Thus Rate α $[B]^1$

Hence overall order of rate is given by

Rate α $[A]^1[B]^1$

Or $\boxed{\text{Rate} = k[A]^1[B]^1}$

Thus overall order of reaction is $1 + 1 = 2$

Q21. Some reaction taking place around room temperature have activation energies around 50 kJ mol^{-1}.

(i) What is the value of the factor $e^{-\frac{E_a}{RT}}$ at 25°C.

Solution:

$E_a = 50\ kJ\ mol^{-1} = 50000\ J\ mol^{-1}$
$T = 25°C + 273 = 298\ K$
$R = 8.314\ J\ mol^{-1}K^{-1}$

Thus

$$e^{-\frac{50000}{8.314 \times 298}} = e^{-20.181} = \boxed{1.72 \times 10^{-9}}$$

(ii) Calculate this factor at 35°C and 45°C and note the increase in this factor for every 10°C rise in temperature.

Solution:

At 35°C

$E_a = 50\ KJ\ mol^{-1} = 50000\ J\ mol^{-1}$
$T = 35°C + 273 = 308\ K$

$R = 8.314\ J\ mol^{-1}K^{-1}$

$$e^{-\frac{50000}{8.314 \times 308}} = e^{-19.52} = \boxed{3.33 \times 10^{-9}}$$

At 45°C

$E_a = 50\ KJ\ mol^{-1} = 50000\ J\ mol^{-1}$
$T = 45°C + 273 = 318\ K$
$R = 8.314\ J\ mol^{-1}K^{-1}$

$$e^{-\frac{50000}{8.314 \times 318}} = e^{-18.91} = \boxed{6.13 \times 10^{-9}}$$

Exponential factor at 25°C = 1.72×10^{-9}
Exponential factor at 35°C = 3.33×10^{-9}
Exponential factor at 45°C = 6.13×10^{-9}

Hence exponential factor doubles for every 10°C rise in T

(iii) Prove that for every 10°C rise in of temperature, the factor doubles and so rate constant also doubles.

Solution:

Rate is given by Arrhenius eq.

$$k = Ae^{-\frac{E_a}{RT}}$$

For a reaction A is almost constant

(write calculations of part (ii) here)

Results of part (ii) shows that, for every 10°C rise in T, exponential factor is doubled.

Hence rate is doubled for every 10°C rise in T.

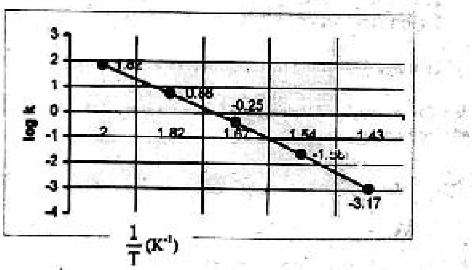
Q24. H_2 and I_2 react to produce HI. Following data for rate constant at various temperatures (K) have been collected.

T (K)	k ($cm^3 mol^{-1} s^{-1}$)
500	6.814×10^{-4}
550	2.64×10^{-4}
600	0.56×10^{-4}
650	7.31×10^{-4}
700	66.67×10^{-4}

(i) Plot a graph between 1/T on x-axis and log k on the y-axis.
(ii) Measure the slope of this straight line and calculate the energy for activation of this reaction.

Solution:

T (K)	k	log k	1/T
500	6.81×10^{-4}	-3.17	2.00×10^{-3}
550	2.64×10^{-2}	-1.58	1.82×10^{-3}
600	5.60×10^{-1}	-0.25	1.67×10^{-3}
650	7.31×10^{0}	0.86	1.54×10^{-3}
700	$6.67 \times 10^{+1}$	1.82	1.43×10^{-3}



From plotted graph Slope $= -8.36 \times 10^{3}$ K

$R = 8.314\ J\ mol^{-1} K^{-1}$

According to Arrhenius equation

$$\log k = \log A - \frac{E_a}{2.303RT}$$

$$\text{slope} = -\frac{E_a}{2.303R}$$

or $E_a = -2.303 \times R \times \text{slope}$

$E_a = -2.303 \times 8.314 \times (-8.36 \times 10^{3})$

$E_a = 160070\ J = \boxed{160.07\ kJ}$

HELLO! Mr. Question here!

Multiple Choice Questions from PAST PAPERS

1. Specific rate constant is equal to rate of reaction, when concentration of reactants are: *(Lahore board, 2014)*
   (a) Zero (b) Four (c) Three (d) Unity
2. The energy of activated complex is: *(Rawalpindi board, 2011)*
   (a) Greater then the reactants & products
   (b) Less than the reactants & products
   (c) Equal to the products
   (d) Equal to the reactants
3. If 75% of any given amount of radioactive element disintegrates in 60 minutes, the half life of radioactive element is: *(Gujranwala board, 2010)*
   (a) 20 minutes (b) 30 minutes (c) 45 minutes (d) 25 minutes
4. Sugar solution hydrolyses to glucose and fructose in the presence of enzyme: *(Gujranwala board, 2008; Multan board, 2010)*
   (a) urease (b) invertase (c) zymase (d) none of these
5. When a reaction proceeds in sequence of steps, the overall rate is determined by: *(Gujranwala board, 2009)*
   (a) fastest step (b) slowest step
   (c) molecularity of all steps (d) order of different steps
6. Arrhenius equation is represented as *(Rawalpindi Board, 2013)*
   (a) $A = Ke^{-E_a/RT}$ (b) $K = Ae^{RT-E_a}$ (c) $A = Ke^{RT-E}$ (d) $K = Ae^{-E_a/RT}$
7. The Hydrolysis of Sugar is catalyzed by: *(Multan Board, 2013)*
   (a) Urease (b) Invertase (c) Zymase (d) Diastase
8. A substance which makes the catalyst more effective is called: *(Lahore Board, 2009, 2010)*
   (a) Inhibitor (b) retarder (c) Promoter (d) Autocatalyst
9. The unit of rate constant for zero order reaction is: *(Faisalabad Board, 2010)*
   (a) $dm^3 s^{-1}$ (b) mole $dm^{-3} s^{-1}$ (c) dm^3 $mole^{-1} s^{-1}$ (d) mole s^{-1}
10. The rate of a chemical reaction is independent of: *(Bahawalpur Board, 2010)*
    (a) Molecularity (b) Temperature
    (c) nature of reactants (d) concentration of reactant
11. The half life period of C_6^{14} is 5760 years. 100 mg of sample of C_6^{14} will reduce to 25 mg in *(Rawalpindi Board, 2010)*
    (a) 11520 years (b) 2880 years (c) 576600 years (d) 5760 years
12. The equation $K = Ae^{-E_a/RT}$ is called *(D.G. Khan Board, 2010)*
    (a) Rate law (b) Rate equation
    (c) Arrheneous equation (d) general gas equation

13. A substance which make the catalyst more effective is called **(Lahore Board, 2011)**
(a) promoter (b) Inhibitor (c) Retarder (d) Poison

14. The order of reaction for the reaction $NO + O_3 \longrightarrow NO_2 + O_2$ is **(Faisalabad Board, 2011)**
(a) two (b) three (c) one (d) zero

15. The minimum amount of energy required for an effective collision is called **(Lahore Board, 2007)**
(a) Activation energy (b) Internal energy
(c) Translational energy (d) None of these

16. With increase of 10°C temperature, the rate of reaction becomes double. This increase in rate of reactions due to **(Faisalabad Board, 2007)**
(a) decrease in the activation energy of reaction
(b) decrease in number of collision between the molecules
(c) increase in activation-energy of reactants
(d) increase in number of effective collisions.

17. Normal human body temperature is **(Lahore Board, 2011)**
(a) 37°C (b) 98.6°C (c) 37°C (d) 273 K

18. The unit of rate constant depends on **(Sargodha Board, 2010)**
(a) order of reaction (b) molecularity (c) number of reactants (d) all of above

19. The rate of reaction determined at any given time is called **(Sargodha Board, 2013)**
(a) instantaneous rate (b) average rate (c) both (d) none

20. Velocity constant is the rate of reaction when the concentrations of the reactants are **(Sargodha Board, 2014)**
a) zero (b) unity (c) two (d) three

Answers to Multiple Choice Questions from Past Papers.

Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans	Q#	Ans
1	(d)	2	(a)	3	(b)	4	(b)	5	(b)
6	(d)	7	(b)	8	(c)	9	(b)	10	(a)
11	(a)	12	(c)	13	(a)	14	(a)	15	(a)
16	(d)	17	(a)	18	(a)	19	(a)	20	(b)

SHORT & LONG QUESTIONS FROM PAST PAPERS

CHEMICAL KINETICS, RATE OF REACTION

Short Questions

(1) *What do you mean by chemical kinetics?* **(Gujranwala Board, 2008)**
(2) *What is meant by rate of reaction? Describe graphically.* **(Multan Board, 2009; Azad Kashmir Board, 2012)**
(3) *Define rate of chemical reaction and give its units.* **(Lahore Board, 2012)**
(4) *Define reaction kinetics and rate of reaction.* **(Bahawalpur Board, 2012)**
(5) *Define instantaneous and average rate of reaction.* **(Bahawalpur Board, 2012)**
(6) *Differentiate between average and instantaneous rate of reaction.* **(Lahore Board, 2008; Bahawalpur Board, 2009; Sargodha Board, 2010, 2013, 2014; Rawalpindi Board, 2013; Multan Board, 2013)** *Define specific rate constant.* **(Lahore Board, 2013)**
(7) *Differentiate between rate and rate constant of a reaction.* **(Faisalabad Board, 2007; Bahawalpur Board, 2008, 2011)**

Long Questions

(1) *Define (i) Rate of reaction (ii) Specific rate of a reaction (iii) Order of a reaction.* **(Rawalpindi Board, 2009; Faisalabad Board, 2011)**

ORDER OF REACTION

Short Questions

(1) *Define order of reaction with examples.* **(Lahore Board, 2011, 2014; Azad Kashmir Board, 2012)**
(2) *What is a zero order reaction?* **(Faisalabad Board, 2008)**
(3) *What is a pseudo first order reaction?* **(D.G. Khan Board, 2010)**
(4) *Define rate of reaction and order of reaction.* **(Faisalabad Board, 2013)**
(5) *How the mechanism of a chemical reaction can help to point out the rate of determining step?* **(Rawalpindi Board, 2007)**

Long Questions

(1) *Explain with one example first order, second order, third order and pseudo first order reaction.* **(Bahawalpur Board, 2010)**

ENERGY OF ACTIVATION

Short Questions

(1) *Define energy of activation. What is the effect of temperature on the activation energy of a reaction.* **(Faisalabad Board, 2008; D.G. Khan Board, 2011)**
(2) *Define (a) Activation energy, (b) Activated complex* **(Multan Board, 2008; Bahawalpur Board, 2010; Faisalabad Board, 2012)** OR *Under what conditions an activated complex is formed?* **(Bahawalpur Board, 2012)**
(3) *What is energy of activation? What is its significance?* **(Rawalpindi Board, 2010)**

Long Questions

(1) *Write a brief note on energy of activation. Explain with graphs.* **(Faisalabad Board 2007; Azad Kashmir Board, 2012; Multan Board, 2013; Gujranwala Board, 2013)**
(2) *What is energy of activation? Discuss Collision theory?* **(Sargodha Board, 2011)**
(3) *What is collision theory of chemical reactions?* **(Rawalpindi board 2007)**

DETERMINATION OF ORDER OF REACTION, RATE DETERMINING STEP

Short Questions

(1) *Write names of any four methods for finding out order of reaction.* **(Bahawalpur Board, 2010)**

(2) Define order of reaction. Write the names of two methods which are used to determine the order of reaction. **(Rawalpindi Board, 2010)**

(3) What is half-life method for the determination of order of a reaction? **(Lahore Board, 2010)**

(4) Write rate equation for the following reactions: **(Gujranwala Board, 2012)**

(a) $NO + O_3 \rightarrow NO_2 + O_2$

(b) $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

(5) What is meant by half-life period (or time)? Give one example. **(Multan Board, 2007, 2010)**

(6) Compare order of reaction and molecularity. **(Sargodha Board, 2012)**

Long Questions

(1) Define order of reaction. Name various methods for its determination and explain half life method in detail. **(Gujranwala Board, 2008, 2009: D.G. Khan Board, 2010: Lahore Board, 2011: Faisalabad Board, 2013)**

(2) What is order of reaction. Describe two methods for finding order of reaction. **(Gujranwala Board, 2011)**

(3) What is order of reaction. Describe the methods for finding the order of reaction. **(Multan Board 2010)**

(4) Define half life period and derive the relation between half-life and order of reaction. **(Rawalpindi Boar,d 2010)**

FACTORS AFFECTING RATE OF REACTION (NATURE, CONC., LIGHT, SURFACE AREA)

Short Questions

(1) Name factors which affect the rate of reaction. **(D.G. Khan Board, 2009; Rawalpindi Board, 2008)**

(2) How surface area affects the rate of a chemical reaction? **(Faisalabad Board, 2010, 2012: Gujranwala Board, 2013)**

(3) How light affects the rate of reaction? **(Sargodha Board, 2010)**

(4) Why light speed up the reaction between H_2 and Cl_2? **(D.G. Khan Board, 2011)**

Long Questions

(1) On which factors rate of chemical reaction depend and explain the effect of concentration of reactants. **(D.G. Khan Board 2012)**

(2) Discuss the factors which influence the rate of chemical reactions. **(D.G. Khan Board 2007, 2012: Multan Board, 2011: Faisalabad Board, 2010, 2012)**

(3) Discuss three important factors influencing the rate of reaction. **(Lahore Board, 2007: Multan Board, 2011)**

(4) How rate of reaction depends upon the following factors : (i) Nature of reactants (ii) Surface area. **(Lahore Board, 2014)**

EFFECT OF TEMPERATRUE ON RATE OF REACTION: ARRHENIUS EQUATION

Short Questions

(1) Briefly explain how higher temperature increase rate of reaction? **(Bahawalpur Board, 2009)**
OR Explain the effect of temperature on rate of a chemical reaction. **(Gujranwala Board, 2009)**

Long Questions

(1) Explain the effect of temperature on rate of reaction. **(Faisalabad Board, 2009)**

(2) How does Arrhenius equation help us to calculate the energy of activation of a reaction? **(Bahawalpur Board, 2009: Lahore Board 2012, 2013)**

(3) How Arrhenius equation explains the effect of temperature on the rate constant of a reaction? **(Sargodha Board, 2010)**

CATALYST, CATALYSIS

Short Questions

(1) Define heterogeneous catalysis with example. **(Sargodha Board, 2013)**

(2) Define homogeneous and heterogeneous catalysis with examples. **(Sargodha Board, 2007: Multan Board, 2011)**

(3) What is catalysis? Give its two types and examples. **(Multan Board, 2007: Lahore Board, 2008: D.G. Khan Board, 2009: Rawalpindi Board, 2009: Lahore Board, 2011)**

(4) Describe two characteristics of a catalyst. **(Sargodha Board, 2013)**

(5) A finely divided catalyst may prove more effective. Give reason. **(Lahore Board, 2009: D.G. Khan Board, 2012)**

(6) What is catalytic poisoning? Give examples **(D.G. Khan Board, 2008, 2010: Rawalpindi Board, 2012)**

(7) What is a promoter or activator? Give an example. **(D.G. Khan Board, 2008: Faisalabad Board, 2009)** **OR** What is activation of a catalyst? Give two examples. **(Faisalabad Board, 2010: D.G. Khan Board, 2012: Lahore Board, 2013)**

(8) Define negative catalyst a long with an example. **(D.G. Khan Board, 2007: Gujranwala Board, 2008: Rawalpindi Board, 2011: Multan Board, 2012)**

(9) What is autocatalyst? Give one example. **(Gujranwala Board, 2011, 2013: Rawalpindi Board, 2012: Sargodha Board, 2014)**

Long Questions

(1) What is homogeneous catalysis? Give two examples. **(Sargodha Board, 2009)**

(2) Differentiate between Homogeneous catalysis and Heterogeneous catalysis with examples. **(D.G. Khan Board, 2009: Lahore Board, 2010: Sargodha Board, 2014)**

(3) Write a brief note on the following :
(i) Homogeneous catalysis. (ii) Heterogeneous catalysis. **(Lahore Board, 2014)**

(4) What is catalysis? Write down its types and explain any one of them **(Bahawalpur Board, 2011: Multan Board, 2012: Sargodha Board, 2013)**

(5) What do you mean by catalytic poisoning of catalyst? Give examples (02 marks)

(6) Write four characteristics of a catalyst. **(Gujranwala Board, 2014)**

ENZYME CATALYSIS

Short Questions

(1) What are enzymes? Give two examples in which enzymes act as catalyst. **(Lahore Board, 2010: D.G. Khan Board, 2012)** OR Give hydrolysis reactions of urea and glucose. **(Bahawalpur Board, 2008: Multan Board, 2009)**

(2) What are enzymes? How enzymes act as a catalyst? **(Faisalabad Board, 2011: Lahore Board, 2013)**

(3) Write down any two characteristics of enzyme catalysis. **(Rawalpindi Board, 2011: Faisalabad Board, 2013: Lahore Board, 2014)** OR Write down any four characteristics of enzyme catalysis **(Multan Board, 2013)**

(4) Define: (i) Catalytic poisoning (ii) enzyme catalysis **(Faisalabad Board, 2007)**

Long Questions

(1) What are enzymes? Explain how do they act as catalysts. **(Lahore Board, 2009, Rawalpindi Board, 2014)**

(2) What are enzymes? Give two examples in which they act as catalyst. **(Multan Board, 2009)**

(3) What is enzyme catalysis. Give an example. Also give four characteristics of enzyme catalysis. **(D.G. Khan Board, 2011: Sargodha Board, 2012)**

TEST YOUR SKILLS

OBJECTIVE

Time: 20 Minutes **Marks: 17**

Note: Over writing, cutting, erasing, using lead pencil will result in loss of marks.

Q1. Each question has four possible answers. Choose the correct answer and encircle it.

(i) The catalyst used for the reaction $HCOOH \rightarrow H_2 + CO_2$
(a) Copper (b) Alumina (c) Silica (d) Iron

(ii) The unit of rate constant 'k' for a first order reaction are?
(a) s^{-1} (b) mol $dm^{-3}s$ (c) mol $dm^{-3}s^{-1}$ (d) $mol^{-1}dm^{3}s$

(iii) When a reaction occurs in many steps than the slowest step is.
(a) Mechanism determining step. (b) Rate determining step.
(c) Enthalpy determining step. (d) None

(iv) The rate of reaction between two specific time intervals is called.
(a) Rate of a reaction (b) Average rate of a reaction.
(c) Instantaneous rate of reaction. (d) None

(v) Dilatometer method is useful for the reactions that involve.
(a) Ionic species (b) Where reactant absorb U.V visible or infrared radiation.
(c) Small volume changes in solution (d) Change in refractive indices.

(vi) The energy of activation of forward reaction is less than that of backward reaction in.
(a) Endothermic reactions (b) Exothermic reaction. (c) Isothermic reaction (d) None

(vii) When NaOH solution reacts with aluminum in different physical states, most rapid reaction occurs with.
(a) Al foil (b) Cubes of Al (c) Al powder. (d) Alloy of Al

(viii) The substance that alters the rate of a chemical reaction but recovered unchanged at the end is called.
(a) Reactant (b) Product (c) Catalyst (d) None

(ix) If the rate of reaction becomes four time when the conc. of reactant A is doubled, keeping concentrations of other reactants constant. Then the order of reaction w.r.t. A will be
(a) 4 (b) 2 (c) 3 (d) 1

(x) Urease enzyme catalyze the hydrolysis of
(a) urea (b) methyl urea (c) ethyl urea (d) all

(xi) Sugar solution hydrolyses to glucose and fructose in the presence of enzyme
(a) urease (b) invertase (c) zymase (d) none of these

(xii) The Unit of rate of reaction is
(a) mole dm^{-3} (b) mole kg^{-1} (c) moles dm^{-3} sec^{-1} (d) grams dm^{-3}

(xiii) Sum of exponents of the concentration terms in the rate equation is called
(a) rate of reaction (b) order of reaction (c) specific rate (d) active mass of reactants.

(xiv) The average rate ad instantaneous rate of a reaction are equal
(a) in the beginning (b) at the end (c) when the time interval of two rates is zero (d) when molar concentrations of reactants are unity.

(xv) For the reaction $2FeCl_3 + 6KI \rightarrow 2FeI_2 + 6KCl + I_2$ the order of the reaction is 3. Its rate equation will be
(a) rate = $K[FeCl_3][KI]^2$ (b) rate = $K[FeCl_3]^2[KI]$
(c) rate = $K[Fe^{+3}][Cl^{-1}][KI]$ (d) rate = $K[KI]^3[FeCl_3]^\circ$

(xvi) Half life period of a reaction is inversely proportional to the initial concentration of the reactant, the order of reaction is
(a) third order (b) second order (c) first order (d) zero order

(xvii) The unit of rate constant depends on
(a) order of reaction (b) molecularity (c) number of reactants (d) All of above

SUBJECTIVE

Time: 2:10 Hours **Marks: 68**

Note: Out of Questions 2,3 and 4, Write any TWENTY TWO(22) short answers. While writing answers write question number carefully. **(22x 2)=44**

Section – I

Q2. Answer any Eight parts from the followings.

(i) Why arsenic purifier is used in the manufacture of H_2SO_4 using Pt catalyst?
(ii) What is difference between instantaneous and average rate of reaction?
(iii) Rate of a chemical reaction increases with increase in temperature. Why?
(iv) How will you calculate the slope of line from Arrhenius plot?
(v) All the collisions among molecules do not give products. Why?
(vi) Half-life time for the disintegration of $^{235}_{92}U$ is a constant quantity. Why?
(vii) Instantaneous rate of reaction is more than average rate at the start of reaction but less at the end of reaction. Why?
(viii) How light affects the rate of reaction?
(ix) Differentiate between homogenous and heterogeneous catalysis.
(x) Enzymes are highly specific in their action. Explain
(xi) What is the rate determining step?
(xii) How does a catalyst work ?

Q3. Answer any Eight parts from the followings.

(i) What is half life period ?
(ii) Define specific rate constant. What is the effect of temperature on it?
(iii) Give examples of zero order reactions?
(iv) How does order of reaction is related to the half life period?
(v) Name the techniques to determine the order of a reaction?
(vi) What is energy of activation?
(vii) Redox reactions are slower than ionic reactions. Why?
(viii) How does rate of combustion of a compound is changed in air and in pure oxygen?
(ix) What is the effect of temperature on the activation energy?
(x) What type of graph is obtained when it is plotted between 1/T on x-axis and log k on y-axis?
(xi) What is catalyst and catalysis?
(xii) Differentiate between homogeneous and heterogeneous catalysis?

Q4. Answer any Six parts from the followings.

(i) What is negative catalyst. Given an example?
(ii) What happens to ethyl alcohol when passed over Al_2O_3 and hot copper separately?
(iii) What is promoter or activator?
(iv) What is autocatalysis?
(v) Write down the reaction in which enzyme urease is used?
(vi) What is the mechanism of enzyme action?
(vii) How is the catalytic activity of enzyme enhanced?
(viii) How does surface area affect the rate of reaction?
(ix) How does temperature affect the role of a catalyst?

Section – II (Attempt any three questions) (8x 3)=24

Q5. (a) What are the characteristics of enzyme catalysis? (04)
(b) What is energy of activation? Discuss collision theory? (04)

Q6. (a) What are pseudo first order reactions? Give example. (02)
(b) A catalyst is required in small amount. Why? (03)
(c) Some reaction taking place around room temperature have activation energies around 50 kJ mol^{-1}. What is the value of the factor $e^{-E_a/RT}$ at 25°C, 35°C and 45°C? (03)

Q7. (a) How arrhenius equation explains the effect of temperature on the rate constant of a reaction? (04)
(b) In the reaction of NO and H_2, it was observed that equimolecular mixture of gases at 340.5 mm pressure was half changed in 102 seconds. In another experiment with an initial pressure of 288 mm of Hg, the reaction was half completed in 140 seconds. Calculate the order of reaction. (04)

Q8. (a) How will you find the order of reaction by half life method. (04)
(b) Explain second and third order reactions with examples? (04)

Q9. (a) How rate of a reaction can be determined? Explain with example (05)
(b) Define the following terms with examples. (03)
(i) Catalyst for a catalyst (ii) Negative catalysis (iii) Autocatalysis

MODEL PAPER
PUNJAB BOARDS OF INTERMEDIATE AND SECONDARY EDUCATION

Total marks: 17 **Paper Code______** **Time Allowed: 20 minutes**

Note:- You have four choices for each objective type question as A, B, C and D. The choice which you think is correct: fill that circle in front of that question number. Use marker or pen to fill the circles. Cutting or filling two or more circles will result in zero mark in that question.

Q.No	Question	A	B	C	D
1	Empirical formula of Glucoses	C_2HO	CH_2O	CHO_2	C_2H_2O
2	The number of molecules present in 9.0 gm of pure water are	3.01×10^{23}	6.02×10^{23}	9.03×10^{23}	1.20×10^{24}
3	The drying agent used in a desiccator is	Lithium Chloride	Sodium Chloride	Potassium Chloride	Calcium Chloride
4	The highest temperature at which a substance can exist as liquid, is called its	Absolute	Consolute	Critical Temperature	Transition Temperature
5	The boiling point of water at Mount Everest is	69oC	74°C	79°C	84°C
6	The existence of an element in more than one crystalline forms is known as	Isotropy	Aniosotropy	Entropy	Allotropy
7	The Scientist Chadwick in 1932 discovered	Proton	Neutron	Electron	Positron
8	The values of Quantum numbers for 3P orbital are	$n = 1, l = 1$	$n = 2, l = 1$	$n = 3, e = 1$	$n = 3, l = 2$
9	The compound which follows octect rule for bonding is	NaCl	BCl_3	PF_5	SF_6
10	The Highest percentage of ionic character is in	HF	HCl	HBr	HI
11	The amount of heat absorbed when one mole of gaseous atoms are formed from the element under standard conditions is called	Enthalpy of Formation	Enthalpy of atomization	Enthalpy of reaction	Enthalpy of combustion
12	In Haber's process, the maximum yield of ammonia can be obtained by	Increasing Pressure	Decreasing pressure	Increasing volume	Increasing temperature
13	The salt dissolved in water forms a solution with pH greater than 7 is	NaCl	Na_2CO_3	$CuSO_4$	NH_4Cl
14	The elevation of boiling point of 0.1 molal solution is	0.0052°C	0.052°C	0.52°C	5.2°C
15	The oxidation number of Oxygen in OF_2 is	+1	−1	+2	−2
16	In Lead Accumulator cell, the electrolyte used is	20 % H_2SO_4	30 % H_2SO_4	40 % H_2SO_4	50 % H_2SO_4
17	Sucrose is converted into Glucose & fructose by enzyme catalyst called	Invertase	Maltase	Urease	Zy...ase

Model Paper Chemistry Subjective

Intermediate Part – I (11th Class) Examination Session 2015-2016 and onward

Total marks: 83 Time: 3:10 hours SECTION —— I

2. Answer any Eight parts from the following:- **8 × 2 = 16**

(i) The removal of an electron from a neutral atom is an endothermic process. Explain with reason.

(ii) Actual yield is always less than theoretical yield. Give two reasons.

(iii) Calculate the no. of molecules present in 34 g of H_3PO_4.

(iv) Solvent extraction ferns the Distribution Law. Justify.

(v) Define sublimation. Give one example.

(vi) Calculate the value of General Gas constant in SI units.

(vii) Pilots feel uncomfortable breathing at higher attitude. Give reason.

(viii) Gases deviate from ideal behaviour at low temperature and high pressure. Give reasons.

(ix) Table salt is an insulator in solid state. Justify.

(x) Liquid crystals can be used in diagonosis of Cancer. Explain.

(xi) Evaporation is a cooling process. Give reason.

(xii) Graphite has slippery touch: Give reason.

3. Answer any Eight parts from the following:- **8 × 2 = 16**

(i) Positive rays are also called canal rays. Give reason.

(ii) The radius of first orbit of hydrogen atom is 0.529 A°. Calculate the radius of 3rd orbit of hydrogen atom

(iii) Explain stark effect.

(iv) Pressure can effect the production of Cathode Rays

(v) Dipole moment of CO_2 is zero. While that of $H2_0$ is 1.85 D. Explain.

(vi) Explain the geometry of H_2Se molecule

(vii) Electronegativity increases from left to right in periodic table. Give reason

(viii) Sketch the molecular orbital picture of O_2

(ix) Enthalpy is a state function. Justify

(x) Born Haber's Cycle is another form of Hess's Law. Justify.

(xi) Buffers are important in many areas of Chemistry. Justify

(xii) Define Le-Chatelier's principle

4. Answer any Six parts from the following:- **6 × 2 = 12**

(i) Give the applications of the solubility product

(ii) Depression of freezing point is a colligative property. Justify.

(iii) $Na_2SO_4 \cdot 10H_2O$ shows discontinuous solubility curve. Give reason.

(iv) What is the molality of a solution prepared by dissolving 5 g of Glucose in 250g of water.

(v) Electromotive force can be calculated from electrochemical series. Explain with reason.

(vi) Lead accumulators is a chargeable battery. Comment.

(vii) Calculate the oxidation number of chromium in; (a) K_2CrO_4 (b) $K_2Cr_2O_7$

(viii) Differentiate between average and instantaneous rate of reaction.

(ix) Explain auto-catalysis.

SECTION — II

Note: Attempt any three questions. (8 x 3 = 24)

5.(a) What are London forces. Explain various factors affecting it. 4

(b) Mg reacts with HCl to give hydrogen gas. What is the minimum volume of HCl solution (27 % by weight) required to produce 16.1g of H2. The density of HCl solution is 1.14 g/cm³.

$Mg(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2(g)$ 4

6.(a) What is hybridization? Explain Sp2 hybridization with example. 4

(b) State first law of thermodynamics and prove that $\Delta E = qv$ 4

7.(a) What is Plasma? How is it produced? Give its two applications. 4

(b) Describe Milikian's Oil Drop method for the measurement of charge of an electron. 4

8. (a) What is Standard Hydrogen Electrode (SHE)? How is it used for the measurement of electrode potential. 4

(b) Calculate the pH of a buffer solution in which 0.11 M CH_3COONa and 0.09 M. acetic acid solutions are present. Ka for CH_3COOH is 1.85×10^{-5}. 4

9. (a) Explain Roult's Law when both components are volatile. 4

(b) Define order of reaction. How does half life method can be used for its determination. 4

APPENDIX A

Table C-1 The SI Unit System

Physical quantity	Name in units	Symbol	Physical quantity	Name in units	Symbol
Length	meter	m	Volume	litre	L ($10^{-3}m^3$)
Mass	kilogram	kg	Length	angstrom	A° (0.1nm)
Time	second	s	Pressure	atmosphere torr	atm(101.325kPa) mmHg(133.32Pa)
Temperature	Kelvin	K	Energy	calorie electron volt	cal (4.184J) eV (1.602×10^{-19}J)
Electrical current	ampere	amp	Temperature	degree celsius	°C (K-273.15)
Luminous intensity	candela	cd	Concentration	molarity	M (mol/L or mol/dm³)
Amount of substance	mole	mol			

Table C-2 Fraction and Multiplies for use in SI

Fraction and Multiplies for Use SI

exa, E	10^{18}	deci, d	10^{-1}
peta, P	10^{15}	centi, c	10^{-2}
tera, T	10^{12}	milli, m	10^{-3}
giga, G	10^{9}	micro, μ	10^{-6}
mega, M	10^{6}	nano, n	10^{-9}
kilo, k	10^{3}	pico, p	10^{-12}
hecto, h	10^{2}	femto, f	10^{-15}
deka, da	10^{1}	atto, a	10^{-18}

Table C-3 Common Derived Units in SI

Physical Quantity	Name of unit	Symbol
Energy	joule	J (kg-m²/s²)
Frequency	hertz	Hz (cycles / s)
Force	newton	N (kg-m/s²)
Pressure	pascal	P (N / m²)
Power	watt	W (J / s)
Electrical charge	coulomb	C (amp-s)
Electrical potential	volt	V (J / c)
Electrical resistance	ohm	Ω (V / amp)
Electrical conductance	siemens	S (amp / V)
Electrical capacitance	farad	F (C / V)

Table C-4 Values of Selected Fundamental Constants

Speed of light in a vacuum (c)	$c = 2.99792458 \times 10^{8}$ m/s
Charge on an electron (q_e)	$q_e = 1.6021892 \times 10^{-19}$ C
Rest mass of electron (m_e)	$m_e = 9.109534 \times 10^{-28}$ g $m_e = 5.4858026 \times 10^{-4}$ amu
Rest mass of proton (m_p)	$m_p = 1.6726485 \times 10^{-24}$ g $m_p = 1.00727647$ amu
Rest mass of neutron (m_n)	$m_n = 1.6749543 \times 10^{-24}$ g $m_n = 1.00865012$ amu
Faraday's constant (F)	F = 96.484.56 C/mol
Planck's constant (h)	$h = 6.626176 \times 10^{-34}$ J-s
Ideal gas constant (R)	R = 0.0820568 L-atm/mol-K R = 8.31441 J/mol-K
Atomic mass unit (amu)	1 amu = $1.6605655 \times 10^{-24}$ g
Boltzmann's constant (k)	$k = 1.380662 \times 10^{-23}$ J/K
Avogadro's constant (N_A)	$N_A = 6.022045 \times 10^{23}$ mol^{-1}
Rydberg constant (R_H)	$R_H = 1.09737318 \times 10^{7} m^{-1}$ $= 1.09739318 \times 10^{7} nm^{-1}$
Molar volume of a gas at STP	$V_m = 2.24 \times 10^{-2} m^3 mol^{-1}$
Heat capacity of water	C = 75.276 J/mol-K

Table C-5 Selected Conversion Factors

energy	1 J = 0.2390 cal = 10^{7} erg 1 cal = 4.184 J 1 ev/atom = $1.6021892 \times 10^{-19}$ J/atom = 96.484 kJ.mol
Temperature	K = °C + 273.15 C = 5/9 (F-32) F = 9/5 (°C) + 32
Pressure	1 atm = 760 mmHg = 760 torr = 101.325 kPa
Mass	1 kg = 2.2046 lb 1lb = 453.59 g = 0.45359 kg 1oz = 0.06250 lb = 28.350 g 1 ton = 2000 lb = 907.185 kg 1 tonne (metric) = 1000 kg = 2204.62 lb
Volume	1 mL = 0.01 L = 1 cm^3 1oz (fluid) = 0.031250 qt = 0.029573 L 1qt = 0.946326 L 1 gal = 0.946 L
Length	1 mile = 1.60934 km 1 in. = 2.54 cm 10mm = 1 cm 1000mm = 1 m 1000m = 1 km 1 m = 39.370 in. A° = 10^{-10} m = 10^{-8} cm